Organometallics 1992, *11*, 2251-2262

Nonlinear Substituent Interactions and the Electron Richness of Substituted (η^6-Arene)Cr(CO)$_3$ Complexes As Measured by IR and ^{13}C NMR Spectroscopy and Cyclic Voltammetry: Role of π-Donor and π-Acceptor Interactions[1,2]

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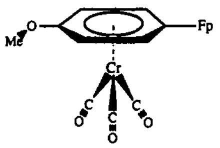
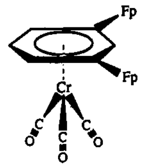
Received November 29, 1991

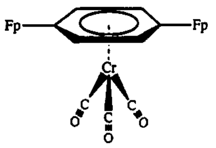
The spectroscopic characterization and oxidative electrochemical behavior (stationary Pt-bead electrode, CH_2Cl_2, $[n\text{-}Bu_4N]PF_6$) of a series of 63 (η^6-arene)Cr(CO)$_3$ complexes having between zero and six substituents on the arene ring (i.e. NEt_2, NMe_2, NH_2, OMe, F, Cl, Me, $SiMe_3$, CO_2Me, C(O)Me, CF_3) with various substitution geometries are reported. The incremental effect of the substituents upon the electron richness of the complexes, as measured by the formal oxidation potentials, $E°'$, the IR carbonyl stretching frequencies and force constants, K_{CO}, and the ^{13}C NMR chemical shifts of the carbonyl ligands, δ_{CO}, is nonlinear and is found to be dependent upon both the electron richness of the chromium center and the substitution geometry about the arene ring. It is proposed that the origin of these nonlinearities lies principally in π-donor and π-acceptor interactions between the substituents on each arene and between each of the substituents on the arene and the chromium center in each complex. Evidence is also provided that the stability of the radical cations of these complexes is dependent upon the electron richness of the metal centers. A valence bond rationale for these effects is provided, and the relationship between these results and the degree of arene planarity and Cr–CO and CrC–O bond lengths of these complexes is discussed.

Introduction

The central goal of our work is the synthesis and characterization of low molecular weight complexes having structures similar to the repeat units of organometallic polymers.[3] In this context, we have prepared and characterized a series of complexes, e.g.







having (η^5-C_5H_5)Fe(CO)$_2$, Fp, groups σ-bonded to arene rings and Cr(CO)$_3$ centers π-bonded to these rings.[3a,4] During the course of these studies, we noted a number of anomalies in the structural, spectroscopic, and electrochemical data of these organometallic derivatives compared to our expectations which were based on the well-developed chemistry of conventional (η^6-arene)Cr(CO)$_3$ complexes having only main-group substituents.[1b,5-9] Thus, during our X-ray crystallographic characterization of one of these species, (η^6-1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$,[3a,4a] we noticed that the arene was very nonplanar and adopts a crownlike geometry with the Fp groups and the ipso-carbon atoms to which they are attached being bent substantially away from the Cr(CO)$_3$ fragment.[1b,3a,4a] We also observed that the incremental effect on the electron richness of the complex of adding a Fp substituent to the benzene ring (as measured by cyclic voltammetry, for example) was dependent upon both the nature of the other substituents on the arene ring and their relative positions with respect to the added Fp group.[4b,c] Thus, we observed that the more electron rich the initial complex the smaller the incremental effect of each additional Fp group upon the oxidation potential (e.g. the first Fp substituent causes a 230-mV decrease in $E°'$ while the third Fp substituent only causes $E°'$ to decrease by 170 mV).[4b] In addition, we

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(1) (a) Substituent Interactions in η^6-Arene Complexes. 2. (b) For part 1, see: Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. *Organometallics*, in press.

(2) Parts of this work have been presented orally: (a) Hunter, A. D.; Mozol, V.; Santarsiero, B. D. 73rd Canadian Chemical Conference, Halifax, Nova Scotia, Canada, July 1990; Abstract 614 IN-F14. (b) Hunter, A. D.; Chukwu, R.; Mozol, V.; Ristic-Petrovic, D. 200th National Meeting of the American Chemical Society Washington, DC. Aug 1990; Abstract INOR121.

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(7) For papers discussing the ^{13}C NMR spectra of (η^6-arene)Cr(CO)$_3$ complexes, see: (a) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 360–363. (b) Gryff-Keller, A.; Szczecinski, P.; Koziel, H. *J. Organomet. Chem.* **1989**, *372*, 255–230. (c) Szczecinski, P.; Gryff-Keller, A. *Magn. Reson. Chem.* **1988**, *26*, 990–991. (d) Solladie-Cavallo, A.; Suffert, J. *Org. Magm. Reson.* **1980**, *14* (No. 5), 426–430. (e) Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *102*, 6902–6904. (f) Hao, N.; McGlinchey, M. J. *J. Organomet. Chem.* **1978**, *161*, 381–390. (g) Roques, B. P. *J. Organomet. Chem.* **1977**, *136*, 33–37. (h) Price, J. T.; Sorensen, T. S. *Can. J. Chem.* **1968**, *46*, 516. (i) Fletcher, J. L.; McGlinchey, M. J. *Can. J. Chem.* **1975**, *53*, 1525–1529. (j) Tirouflet, J.; Besancon, J.; Mabon, F.; Martin, M. L. *Org. Magn. Reson.* **1976**, *8*, 444–448. (k) Roques, B. P.; Segard, C. *J. Organomet. Chem.* **1974**, *73*, 327–330. (l) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1–25. (m) Thoennes, D. J.; Wilkins, C. L.; Trahanovsky, W. S. *J. Magm. Reson.* **1974**, *13*, 18–26. (n) Cletta, F.; Gambaro, A.; Rigatti, G.; Venzo, A. *Spectrosc. Lett.* **1977**, *10* (12), 971–977.

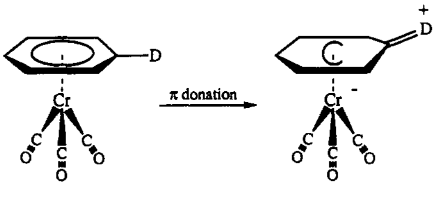
0276-7333/92/2311-2251$03.00/0

observed that the para-substituted isomer of $(\eta^6\text{-}C_6H_4Fp_2)Cr(CO)_3$ appeared to be somewhat more electron rich than was the meta-substituted isomer (by 20 mV).[4b] Finally, we observed that the addition of Fp substituents led to a dramatic stabilization of the chemically or electrochemically generated radical cations of $(\eta^6\text{-arene})Cr(CO)_3$ complexes bearing Fp substituents, e.g.[4b,c]

$$(\eta^6\text{-}C_6H_4Fp_2)Cr(CO)_3 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(\eta^6\text{-}C_6H_4Fp_2)Cr(CO)_3]^{\bullet+} \quad (1)$$

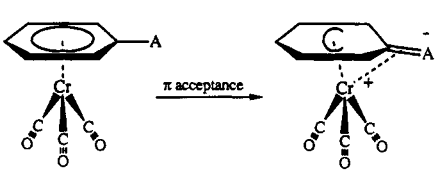
One possible explanation for these effects is that they are caused by direct iron-to-chromium steric and/or electronic interactions. However, consideration of the long Cr–Fe distance in this complex (≈4 Å)[3a] and isolated reports of similar structural and electronic effects having been observed for a few conventional $(\eta^6\text{-arene})Cr(CO)_3$ complexes having strongly π-donating substituents led us to hypothesize that these unusual and apparently anomalous behaviors were a characteristic feature, albeit not widely recognized, of all $(\eta^6\text{-arene})Cr(CO)_3$ complexes. In particular, we felt that this behavior was probably due to the π-donor nature of the Fp substituents.[3b,c,4a,10]

To test this hypothesis, we developed a general model for the electronic interactions between the substituents on these arene rings and the $Cr(CO)_3$ centers.[11] This model emphasizes the importance of π-donor and/or π-acceptor interactions between the arene substituents and the rest of each complex, i.e.



(2)

1a 1b



(3)

2a 2b

(where D is a π-donor such as NMe_2, OMe, or F and A is a π-acceptor such as CO_2Me, C(O)Me, or CF_3), and it has proven remarkably useful in explaining the X-ray crystal structures reported for the substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes.[1b] However, if this model is to have maximal utility, and if it is correct at identifying the underlying causes for these distortions, it should also be able to predict and explain the electron richness of the chromium centers in these substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes as a function of the π-donor and/or π-acceptor character of the substituents. In this paper, we report that our model is successful in this regard. In particular, the IR, NMR, and oxidative electrochemical characterizations of 63 $(\eta^6\text{-arene})Cr(CO)_3$ complexes having between zero and six arene substituents (X = NEt_2, NMe_2, NH_2, OMe, F, Cl, Me, $SiMe_3$, CO_2Me, C(O)Me, CF_3) are reported and the data are rationalized in terms of the above bonding model.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. Reagents and chemicals used were handled by the conventional techniques used for the manipulation of air-sensitive compounds which have been described in detail previously.[3,4] Infrared spectra were recorded as CH_2Cl_2 solutions on a Pye Unicam PU9522 infrared spectrometer and were calibrated with the 1601-cm^{-1} band of polystyrene. The ^1H and ^{13}C NMR spectra were recorded as $(CD_3)_2SO$ solutions on a Bruker AM-300 (or

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(8) For electrochemical investigations of $(\eta^6\text{-arene})Cr(CO)_3$ complexes, see: (a) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1–93. (b) Bond, A. M.; Jaouen, G.; Mann, T. F.; Mocellin, E.; Top, S. *Organometallics* **1989**, *8*, 2382–2387. (c) Zoski, C. G.; Sweigart, D. A.; Stone, N. J.; Rieger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109–2116. (d) Rourke, F.; Crayston, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1264–1266. (e) Bullick, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3084–3086. (f) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553–2555. (g) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819–7824. (h) Ikeshoji, T.; Parker, V. D. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1112–1115. (i) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand. A* **1984**, *38*, 175–178. (j) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand. B* **1983**, *37*, 715–721. (k) Peterleitner, M. G.; Tolstayo, M. V.; Krivykh, V. V.; Denisovitch, L. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1983**, *254*, 313–315. (l) Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* **1983**, *22*, 987–989. (m) Degrand, C.; Radecki-Sudre, A.; Besancon, J. *Organometallics* **1982**, *1*, 1311. (n) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Randovovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938–950. (o) Rieke, R. D.; Milligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* **1981**, *218*, C25–C30. (p) Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *J. Chem. Soc., Dalton Trans* **1975**, 2335–2340. (q) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768–1770. (r) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449–460. (s) Van Order, N.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680–5690. (t) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420–427. (u) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699–705. (v) Leong, V. S.; Cooper, N. J. *Organometallics* **1987**, *6*, 2000–2002. (w) Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6426–6429. (x) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171–173. (y) Ceccon, A.; Gentiloni, M.; Romanin, A.; Venzo, A. *J. Organomet. Chem.* **1977**, *127*, 315–324. (z) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968–3976.

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(11) For a detailed discussion of our π-donor/π-acceptor model and its relationship to the X-ray crystal structures of substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes, see ref 1b.

occasionally AM-400) spectrometer with reference to the deuterium signal employed and are reported in parts per million downfield from external Me_4Si.

Preparation of the (η^6-Arene)Cr(CO)$_3$ Complexes Required for This Work. Most of the (η^6-arene)Cr(CO)$_3$ complexes required for this work (see Table I) have been reported previously,[5] and these species, and the new complexes reported herein, were prepared by conventional methods.[5,12]

Method A. Complexes having relatively electron-poor arenes (i.e. having two or more π-acceptor substituents) were prepared in refluxing Bu_2O as described below using the preparation of (η^6-1,4-$C_6H_4(CO_2Me)_2$)Cr(CO)$_3$ as a representative example.

To a 300-mL round-bottom flask equipped with a gas inlet and an air-cooled condenser[4a] was added $Cr(CO)_6$ (10.00 g, 45.4 mmol), 1,4-$C_6H_4(CO_2Me)_2$ (8.00 g, 41.6 mmol), and Bu_2O (100 mL). The resulting white suspension was refluxed for 55 h, during which time the solution turns red and new IR bands appeared in the carbonyl region at ≈1990 (s) and 1934 (s, br) cm^{-1}. The solution was cooled to ambient temperature, filtered to remove a white solid, and taken to dryness in vacuo. Excess starting materials were removed by sublimation from the solid (at 0.1 Torr) onto a water-cooled probe, and the residual solid was then recrystallized from CH_2Cl_2/hexanes to afford (η^6-1,4-$C_6H_4(CO_2Me)_2$)Cr(CO)$_3$ in 19% yield (2.91 g, 8.81 mmol) as an analytically pure red crystalline solid.[13]

Method B. All of the other complexes were prepared using Bu_2O containing 5–10% THF as the solvent[12a] except for (η^6-1,4-$C_6H_4Cl_2$)Cr(CO)$_3$, which was prepared in dioxane.[12b] The preparation of (η^6-1,4-$C_6H_4(NMe_2)_2$)Cr(CO)$_3$ is described as a representative example.[12a]

To a 250-mL round-bottom flask equipped with a gas inlet and an air-cooled condenser[4a] was added $Cr(CO)_6$ (1.61 g, 7.29 mmol), 1,4-$C_6H_4(NMe_2)_2$ (2.00 g, 12.2 mmol), Bu_2O (120 mL), and THF (10 mL). The resulting white suspension was refluxed for 19 h, during which time the solution turns yellow and new IR bands appeared in the carbonyl region at ≈1951 (s) and 1871 (s, br) cm^{-1}. The solution was cooled to ambient temperature, concentrated in vacuo to ≈100 mL, and then cooled to -35 °C. The resulting yellow crystals were collected on a fritted glass funnel and washed with hexanes to give analytically pure yellow crystals of (η^6-1,4-$C_6H_4(NMe_2)_2$)Cr(CO)$_3$ in 80% yield (1.75 g, 5.83 mmol).[13]

The IR and ^{13}C NMR data for each complex prepared in this work are collected in Table I, while their ^{1}H NMR data have been deposited as supplementary material.

Electrochemical Analysis of the Products. The electrochemical analyses were carried out using the equipment and experimental methods described in detail previously.[3d,4c] Thus, the working electrode was a ≈1-mm-diameter Pt bead, the support electrolyte was [n-Bu_4N]PF_6, and the solvent was dichloromethane (Spectrograde, BDH) which was treated with alumina (ICN Biomedical, neutral, W200 Super 1).[3d,4c] The solutions employed during cyclic voltammetry were typically (5–7) × 10^{-4} M in organometallic complex and 0.1 M in [n-Bu_4N]PF_6, and these experiments were carried out at ambient temperatures (≈23 °C). The cathodic to anodic peak current ratio is defined by $i_{p,c}/i_{p,a}$ and is used throughout the text to establish chemical reversibility, and ferrocene ($E°' = +0.470$ V vs SCE, $i_{p,c}/i_{p,a} = 1.0$, $\Delta E = 60$–70 mV, 0.1 V s^{-1}) or cobaltocene was added as an internal reference after the cyclic voltammetric experiments.[3d,4c,14] The oxidation potential data was found to be reproducible to within at least 3–4 mV, and the formal oxidation potentials are reported in Table I to the nearest millivolt (relative to the aqueous SCE reference electrode).

Results

The 63 new and previously reported (η^6-arene)Cr(CO)$_3$ complexes required for this work (Table I) were prepared by conventional methods, and these syntheses were unexceptional, i.e.[5,12]

$$Cr(CO)_6 + \text{arene} \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-arene})Cr(CO)_3 \qquad (4)$$

$$Cr(CO)_6 + \text{arene} \xrightarrow[Bu_2O\ (5\text{–}10\%\ THF)]{\Delta} (\eta^6\text{-arene})Cr(CO)_3 \qquad (5)$$

These complexes were chosen to have between zero and six substituents with a wide range of π-donor (X = NEt_2, NMe_2, NH_2, OMe, F, Cl, Me) and π-acceptor (X = $SiMe_3$, CO_2Me, C(O)Me, CF_3) strengths and to have a variety of substitution geometries around the arene rings.

The infrared spectra for each of the complexes (Table I) displayed the expected pairs of carbonyl stretching frequencies due to the A_1 and E bands of the Cr(CO)$_3$ units (in the ranges 1946–2003 and 1857–1947 cm^{-1}, respectively)[6,15] and are reported in Table I along with the relative peak widths at half-height of the A_1 and E bands, $\Delta\nu^{1/2}$, i.e.

$$\Delta\nu^{1/2} = \frac{\nu^{1/2}(E)}{\nu^{1/2}(A_1)} \qquad (6)$$

(where $\nu^{1/2}(E)$ and $\nu^{1/2}(A_1)$ are the peak widths at half-height of the E and A_1 bands, respectively), which are found to vary between 2.0 and 3.3.[16] The carbonyl stretching force constants, K_{CO}, calculated by the method of Cotton and Kraihanzel,[15] are also recorded in Table I and were found to range between 14.38 × 10^5 and 15.61 × 10^5 dyn cm^{-1} with the interaction constant, $K_{CO}{}^{i}$, ranging between 0.30 × 10^5 and 0.46 × 10^5 dyn cm^{-1}. These IR data will be used below as one empirical estimate of the electron richness of these complexes. In particular, these data indicate that (η^6-1,4-$C_6H_4(NMe_2)_2$)Cr(CO)$_3$ was the most electron-rich complex characterized in this work (i.e. K_{CO} = 14.38 × 10^5 dyn cm^{-1}), while (η^6-1,3,5-$C_6H_3(CO_2Me)_3$)Cr(CO)$_3$ was the most electron-poor species (i.e. K_{CO} = 15.61 × 10^5 dyn cm^{-1}). Indeed, to the best of our knowledge, the latter complex appears to be the most electron-poor (η^6-arene)Cr(CO)$_3$ complex yet reported.[17]

The ^{1}H and ^{13}C NMR spectra for these complexes are relatively simple due to the high symmetries of the molecules and were assigned using a combination of the peak multiplicities, intensities, chemical shifts, coupling constants, and homo- and heteronuclear decoupling experiments. The ^{1}H NMR data for the complexes and the ^{13}C NMR data for the arene substituents are as expected and have been deposited as supplementary material. The assignments of the ^{13}C NMR spectra of the arene ligands (Table I) were confirmed by comparison of the experimental chemical shifts of the chemical shifts predicted for each carbon by consideration of the characteristic substituent effects of the arene substituents in (η^6-arene)Cr-

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(12) Method B has been described in detail previously, see: (a) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154–158. (b) Alemagna, A.; Cremonesi, P.; Buttero, P. D.; Licandro, E.; Maiorana, S. *J. Org. Chem.* **1983**, *48*, 3114–3116.

(13) The purity and identity of the new complexes prepared for this work were also ascertained by satisfactory elemental analyses (C, H, N) and low-resolution mass spectra.[3b,c] No attempt was made to optimize the yields in these syntheses.

(14) (a) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406. (b) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1980**, *101*, 2038–2044. (c) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

(15) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432–4438.

(16) In fact, linear regression analysis of this data indicates that the relative broadening of the E band increases with the electron richness of the complex.

(17) It has proven extremely difficult to synthesize (η^6-arene)Cr(CO)$_3$ complexes with arene substituents such as NO_2, which are very strong π-acceptors. This is probably due to the oxidizing ability of these arenes and the fact that they are too electron poor to readily displace other ligands in a chromium atom's coordination sphere.

(CO)$_3$ complexes (Table II).[3b,4,7,18] It is noteworthy that there is substantial agreement between the observed and calculated chemical shifts. In fact, the average discrepancy was only 1.6 ppm for the 5 (η^6-1,2-$C_6H_4X_2$)Cr(CO)$_3$ complexes, 1.6 ppm for the 17 (η^6-1,3-$C_6H_4X_2$)Cr(CO)$_3$ complexes, 1.1 ppm for the 21 (η^6-1,4-$C_6H_4X_2$)Cr(CO)$_3$ complexes, 3.1 ppm for the 9 miscellaneous (η^6-arene)Cr(CO)$_3$ complexes (which have from 3 to 6 substituents), and 1.7 ppm for all of the 52 polysubstituted (η^6-arene)Cr(CO)$_3$ complexes studied. The Δ_π values[1b,3b,4] listed for the substituents in Table II are a measure of the net π-donor or π-acceptor character of each substituent. They are being used in preference to conventional Hammett, Taft, etc. substituent parameters,[19] since Δ_π is readily measured for

Table I. IR, ^{13}C NMR, and Electrochemical Data for the Complexes

arene substituents						IR[a]				
X1	X2	X3	X4	X5	X6	ν_{CO}(A), cm^{-1}	ν_{CO}(E), cm^{-1}	$\Delta\nu^{1/2}$[d]	$10^5K_{CO}{}^{i}$, dyn cm^{-1}	10^5K_{CO}, dyn cm^{-1}
H	H	H	H	H	H	1974	1894	2.4	0.42	14.90
NEt_2	H	H	H	H	H	1954	1864	2.5	0.46	14.49
NMe_2	H	H	H	H	H	1956	1868	2.7	0.45	14.54
NH_2	H	H	H	H	H	1962	1877	2.5	0.44	14.67
OMe	H	H	H	H	H	1973	1891	2.5	0.43	14.87
F	H	H	H	H	H	1982	1903	2.0	0.41	15.04
Cl	H	H	H	H	H	1986	1908	2.2	0.41	15.11
Me	H	H	H	H	H	1969	1889	2.2	0.42	14.83
$SiMe_3$	H	H	H	H	H	1968	1890	2.4	0.41	14.83
CO_2Me	H	H	H	H	H	1985	1911	2.3	0.39	15.14
CF_3	H	H	H	H	H	1990	1918	2.2	0.38	15.24
OMe	OMe	H	H	H	H	1965	1881	2.4	0.43	14.72
NH_2	NH_2	H	H	H	H	1954	1866	2.5	0.45	14.51
F	Me	H	H	H	H	1977	1898	2.3	0.41	14.96
Me	Me	H	H	H	H	1965	1883	2.8	0.42	14.74
Me	CO_2Me	H	H	H	H	1980	1906	2.0	0.39	15.06
NH_2	H	NH_2	H	H	H	1952	1862	2.8	0.46	14.46
OMe	H	OMe	H	H	H	1965	1881	2.4	0.43	14.72
Cl	H	Cl	H	H	H	1990	1922	2.3	0.36	15.28
Me	H	Me	H	H	H	1966	1883	2.2	0.43	14.75
CO_2Me	H	CO_2Me	H	H	H	1997	1931	2.8	0.35	15.41
NH_2	H	OMe	H	H	H	1958	1871	2.6	0.45	14.59
NH_2	H	F	H	H	H	1971	1889	2.4	0.43	14.84
NH_2	H	Me	H	H	H	1958	1874	2.5	0.43	14.62
NH_2	H	C(O)Me	H	H	H	1971	1893	2.7	0.41	14.88
NH_2	H	CF_3	H	H	H	1977	1900	2.4	0.40	14.98
OMe	H	F	H	H	H	1966	1888	2.4	0.40	14.80
OMe	H	Me	H	H	H	1966	1883	2.4	0.43	14.75
OMe	H	CO_2Me	H	H	H	1979	1904	2.4	0.39	15.03
F	H	Me	H	H	H	1977	1900	2.1	0.40	14.98
Cl	H	Me	H	H	H	1977	1901	2.1	0.40	14.99
Me	H	CO_2Me	H	H	H	1979	1906	2.3	0.38	15.05
NH_2	H	Cl	H	H	H	1969	1891	2.6	0.41	14.85
NMe_2	H	H	NMe_2	H	H	1946	1857	3.3	0.46	14.38
NH_2	H	H	NH_2	H	H	1954	1868	3.1	0.44	14.53
OMe	H	H	OMe	H	H	1966	1883	2.9	0.43	14.75
Cl	H	H	Cl	H	H	1990	1919	2.2	0.37	15.24
Me	H	H	Me	H	H	1966	1884	2.5	0.42	14.76
CO_2Me	H	H	CO_2Me	H	H	1994	1929	3.0	0.34	15.37
NMe_2	H	H	NH_2	H	H	1949	1864	3.1	0.44	14.47
NH_2	H	H	OMe	H	H	1960	1870	2.8	0.46	14.59
NH_2	H	H	F	H	H	1970	1889	2.6	0.42	14.83
NH_2	H	H	Cl	H	H	1969	1888	2.7	0.42	14.82
NMe_2	H	H	CO_2Me	H	H	1966	1886	2.3	0.41	14.78
Me	H	H	CO_2Me	H	H	1981	1907	2.2	0.39	15.07
NH_2	H	H	Me	H	H	1958	1874	2.6	0.43	14.62
NH_2	H	H	C(O)Me	H	H	1971	1894	2.5	0.40	14.89
NH_2	H	H	CO_2Me	H	H	1971	1894	2.4	0.40	14.89
NH_2	H	H	CF_3	H	H	1977	1898	2.3	0.41	14.96
OMe	H	H	F	H	H	1977	1898	2.8	0.41	14.96
OMe	H	H	Me	H	H	1966	1882	2.3	0.44	14.74
OMe	H	H	CO_2Me	H	H	1980	1905	2.2	0.39	15.05
F	H	H	Me	H	H	1977	1899	2.3	0.41	14.97
Cl	H	H	Me	H	H	1977	1902	2.2	0.39	15.00
OMe	H	OMe	H	OMe	H	1961	1874	2.6	0.45	14.63
Me	H	Me	H	Me	H	1962	1881	2.3	0.42	14.71
CO_2Me	H	CO_2Me	H	CO_2Me	H	2003	1947	2.3	0.30	15.61
NH_2	H	CO_2Me	H	CO_2Me	H	1981	1909	2.6	0.38	15.09
Me	Me	H	Me	H	H	1961	1880	2.5	0.42	14.69
OMe	OMe	OMe	H	H	H	1963	1879	2.4	0.43	14.69
Me	Me	H	Me	Me	H	1957	1871	2.4	0.44	14.58
Me	Me	Me	Me	Me	H	1952	1868	2.3	0.43	14.52
Me	Me	Me	Me	Me	Me	1948	1864	2.4	0.43	14.46

[a] Recorded in CH_2Cl_2. [b] Recorded in $(CD_3)_2SO$. [c] Electrochemical data recorded in CH_2Cl_2 (0.1 M in $[n\text{-}Bu_4N]PF_6$) at a Pt-bead electrode
[e] For chemically irreversible oxidations, $E_{p,a}$ is reported in parentheses (recorded at 0.1 V s^{-1}).

substituents on (η^6-arene)Cr(CO)$_3$ complexes while σ^+, σ^-, etc. are not generally available for complexed arenes.[1b] The ^{13}C NMR chemical shifts for the Cr–carbonyl ligands (Table I) will be used as our second empirical measure of the electron richness of the complexes.[20]

For all of our diverse (η^6-arene)Cr(CO)$_3$ complexes, we observe one-electron electrochemical oxidation processes similar to those previously reported, i.e.

$$(\eta^6\text{-arene})\mathrm{Cr(CO)_3} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(\eta^6\text{-arene})\mathrm{Cr(CO)_3}]^{\bullet+} \qquad (7)$$

for complexes having alkyl substituents or a restricted range of π-donor or π-acceptor substituents.[4b,c,8a,c,e,f,p,q,21] An interesting experimental observation that we made

^{13}C NMR:[b] measd, ppm (calcd, ppm)							electrochemical data[c]		
C1	C2	C3	C4	C5	C6	CO	$E^{\circ\prime}$ ($E_{p,a}$),[e] V	ΔE, mV	$i_{p,c}/i_{p,a}$
95.15	95.15	95.15	95.15	95.15	95.15	234.00	0.877	84	0.91
135.92	74.72	99.30	82.83	99.30	74.72	235.74	0.582	133	0.87
136.16	76.17	98.82	84.14	98.82	76.17	235.52	0.577	73	0.89
137.09	77.57	99.09	82.96	99.09	77.57	235.97	0.589	80	0.92
144.15	80.28	97.48	87.44	97.48	80.28	234.25	0.783	80	0.93
146.82	81.65	96.09	89.42	96.09	81.65	232.98	0.955	98	0.76
113.37	93.59	95.97	91.34	95.97	93.59	232.85	0.987	89	0.75
111.71	96.62	94.79	91.85	94.79	96.62	234.29	0.846	88	0.92
101.08	101.36	93.03	97.69	93.03	101.36	234.16	0.887	154	0.91
91.05	96.04	92.47	97.46	92.47	96.04	231.98	1.027	81	0.78
96.16	92.17	91.43	96.94	91.43	92.17	231.43	1.085	130	0.70
133.86 (129.4)	133.86 (129.4)	80.83 (82.7)	89.19 (89.8)	89.19 (89.8)	80.83 (82.7)	234.75	0.745	92	0.84
119.53 (119.6)	119.53 (119.6)	82.76 (81.6)	87.86 (87.0)	87.86 (87.0)	82.76 (81.6)	238.42	0.464	71	0.90
144.74 (148.3)	97.85 (98.2)	96.98 (97.6)	90.74 (89.1)	94.10 (92.8)	82.72 (81.3)	233.26	0.913	113	0.89
109.82 (113.2)	109.82 (113.2)	97.13 (96.3)	93.93 (91.5)	93.43 (91.5)	97.13 (96.3)	234.69	0.808	100	0.87
113.22 (112.6)	92.33 (92.6)	98.24 (95.7)	90.50 (89.2)	98.33 (97.2)	94.71 (94.0)	232.56	0.968	77	0.83
136.96 (141.4)	67.87 (60.1)	136.96 (141.4)	69.94 (65.5)	98.41 (103.1)	69.94 (65.5)	237.51	0.417	72	0.93
144.89 (146.6)	70.75 (65.5)	144.89 (146.6)	74.91 (72.6)	100.14 (99.9)	74.91 (72.6)	234.53	0.719	80	0.87
114.03 (114.3)	92.38 (92.1)	114.03 (114.3)	90.60 (89.8)	95.38 (96.9)	90.60 (89.8)	231.90	(1.14)	irrev	
112.51 (111.4)	97.42 (98.1)	112.51 (111.4)	92.04 (93.3)	95.47 (94.5)	92.04 (93.3)	234.57	0.819	99	0.92
89.20 (88.5)	95.81 (96.9)	89.20 (88.5)	97.56 (98.4)	90.63 (89.9)	97.56 (98.4)	229.55	1.160	120	0.53
136.88 (139.5)	68.62 (68.2)	145.83 (148.2)	70.71 (68.2)	97.25 (101.5)	73.28 (69.9)	236.12	0.561	87	0.93
135.42 (138.1)	67.29 (64.1)	150.51 (150.8)	71.14 (69.5)	98.88 (100.1)	73.40 (71.9)	235.18	0.675	78	0.82
136.89 (136.8)	79.65 (79.1)	113.72 (115.7)	84.23 (84.5)	96.68 (98.8)	75.70 (74.3)	236.12	0.567	86	0.95
136.69 (136.7)	74.37 (77.1)	102.47 (107.4)	83.84 (82.5)	98.31 (98.7)	78.95 (81.9)	235.28	0.714	66	0.89
136.04 (133.4)	71.09 (74.7)	102.24 (100.1)	79.00 (80.1)	97.65 (95.4)	77.65 (79.4)	234.23	0.755	78	0.95
146.36 (145.2)	71.18 (66.8)	149.90 (149.2)	76.43 (73.9)	96.20 (98.5)	77.00 (74.6)	234.60	0.867	88	0.71
144.54 (143.9)	82.00 (81.8)	113.00 (114.1)	88.44 (88.9)	97.38 (97.2)	78.08 (77.0)	234.55	0.766	91	0.89
142.65 (141.6)	78.76 (81.2)	94.44 (93.5)	88.23 (88.3)	95.97 (94.9)	82.35 (82.7)	233.01	0.941	86	0.69
145.76 (145.5)	83.04 (83.1)	112.19 (112.7)	90.18 (90.9)	95.98 (95.8)	79.37 (78.3)	233.35	0.936	69	0.62
114.77 (113.1)	93.96 (95.1)	112.20 (112.6)	91.50 (92.8)	96.54 (95.7)	90.91 (90.3)	233.21	0.956	93	0.80
109.61 (109.1)	95.19 (97.5)	92.86 (90.7)	94.26 (92.7)	93.13 (92.2)	97.15 (99.0)	232.67	0.993	68	0.82
136.60 (138.0)	77.91 (76.1)	117.21 (117.4)	83.19 (81.5)	97.55 (100.0)	75.05 (73.8)	235.01	0.688	79	0.86
127.20 (125.2)	79.55 (79.9)	79.55 (79.9)	127.20 (125.2)	79.55 (79.9)	79.55 (79.9)	237.69	0.390	82	0.96
125.45 (125.0)	80.86 (81.6)	80.86 (81.6)	125.45 (125.0)	80.86 (81.6)	80.86 (81.6)	238.39	0.409	80	0.82
137.31 (136.5)	81.69 (82.7)	81.69 (82.7)	137.31 (136.5)	81.69 (82.9)	81.69 (82.9)	234.83	0.694	82	0.97
108.86 (109.6)	94.11 (94.5)	94.11 (94.5)	108.86 (109.6)	94.11 (94.5)	94.11 (94.5)	231.51	1.055	90	0.63
108.42 (108.4)	96.24 (96.3)	96.24 (96.3)	108.42 (108.4)	96.24 (96.3)	96.24 (96.3)	234.40	0.804	93	0.98
93.37 (93.5)	93.67 (93.4)	93.67 (93.4)	93.37 (93.5)	93.67 (93.4)	93.67 (93.4)	230.73	(1.11)	irrev.	
124.24 (124.1)	78.44 (80.2)	82.12 (81.3)	129.04 (126.1)	82.12 (81.3)	78.44 (80.2)	238.01	0.400	64	0.95
131.15 (129.4)	77.01 (80.0)	85.21 (84.3)	132.88 (132.1)	85.21 (84.3)	77.01 (80.0)	236.61	0.535	68	0.92
133.02 (131.4)	75.03 (78.6)	86.73 (85.6)	136.56 (134.7)	86.73 (85.6)	75.03 (78.6)	235.12	0.646	80	0.90
135.11 (133.3)	76.42 (78.5)	98.38 (97.6)	98.60 (101.3)	98.38 (97.6)	76.42 (78.5)	234.73	0.660	97	0.86
137.84 (138.6)	75.00 (73.6)	98.75 (99.7)	82.44 (80.1)	98.75 (99.7)	75.00 (73.6)	233.17	0.721	74	0.89
113.98 (114.1)	92.74 (94.0)	97.00 (95.7)	88.64 (87.8)	97.00 (95.7)	92.74 (94.0)	232.10	0.955	75	0.82
134.91 (133.8)	77.77 (77.3)	99.61 (100.6)	97.97 (99.6)	99.61 (100.6)	77.77 (77.3)	236.29	0.542	101	0.97
139.49 (141.4)	76.67 (77.2)	98.82 (98.8)	89.41 (91.3)	98.82 (98.8)	76.67 (77.2)	233.64	0.756	75	0.83
139.21 (139.5)	76.58 (75.0)	99.22 (100.0)	81.64 (79.0)	99.22 (100.0)	76.58 (75.0)	233.65	0.730	70	0.84
138.75 (138.9)	74.65 (73.5)	95.61 (96.2)	86.13 (84.0)	95.61 (96.2)	74.65 (73.9)	233.33	0.779	87	0.84
139.02 (138.5)	80.09 (81.3)	83.99 (84.0)	139.85 (139.1)	83.99 (84.0)	80.09 (81.3)	233.39	0.841	87	0.89
141.90 (140.9)	80.95 (80.0)	97.35 (99.0)	103.38 (104.0)	97.35 (99.0)	80.95 (80.0)	234.56	0.745	115	0.99
145.61 (145.6)	78.98 (77.7)	97.32 (98.4)	85.35 (83.4)	97.32 (98.4)	78.98 (77.7)	231.88	0.941	89	0.82
144.68 (143.5)	82.59 (81.3)	95.79 (97.6)	105.91 (106.0)	95.79 (97.6)	82.59 (81.3)	233.26	0.910	87	0.89
109.64 (110.1)	94.88 (93.3)	95.46 (97.5)	108.28 (107.9)	95.46 (97.5)	94.88 (93.3)	233.06	0.930	84	0.91
143.88 (149.0)	66.12 (57.8)	143.88 (149.0)	66.12 (57.8)	143.88 (149.0)	66.12 (57.8)	235.13	0.686	75	0.88
112.75 (111.1)	93.15 (94.8)	112.75 (111.1)	93.15 (94.8)	112.75 (111.1)	93.15 (94.8)	234.86	0.785	106	0.97
88.09 (85.9)	96.34 (99.3)	88.09 (85.9)	96.34 (99.3)	88.09 (85.9)	96.34 (99.3)	227.01	(1.38)	irrev	
130.64 (131.9)	76.45 (80.9)	95.65 (92.5)	(84.8)	95.65 (92.5)	76.45 (80.9)	234.00	0.832	73	0.87
110.12 (109.9)	110.85 (112.9)	98.30 (97.8)	106.55 (108.1)	93.48 (93.0)	97.27 (96.0)	234.94	0.764	91	0.96
140.70 (131.8)	121.57 (114.6)	140.70 (131.8)	71.71 (75.0)	91.89 (92.2)	71.21 (75.0)	234.79	0.704	94	0.80
108.08 (109.6)	108.08 (109.6)	99.34 (97.5)	108.08 (109.6)	108.08 (109.6)	99.34 (97.5)	235.33	0.774	75	0.97
106.74 (109.3)	108.84 (111.1)	110.30 (114.1)	108.84 (111.1)	106.74 (109.3)	97.11 (94.2)	235.58	0.709	82	0.92
107.63 (110.8)	107.63 (110.8)	107.73 (110.8)	107.73 (110.8)	107.73 (110.8)	107.63 (110.8)	235.90	0.668	82	0.92

and at a scan rate of 100 mV s^{-1}. Potentials are reported versus SCE. [d] E band width at half-height divided by A$_1$ band width at half-height.

Table II. Substituent Parameters for the (η^6-C_6H_5X)Cr(CO)$_3$ Complexes

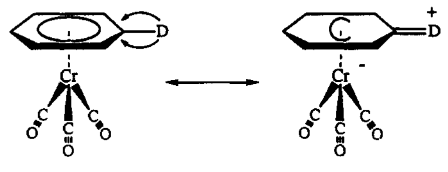
X	Δ_{ipso},[a] ppm	Δ_{ortho},[a] ppm	Δ_{meta},[a] ppm	Δ_{para},[a] ppm	Δ_π,[b] ppm	σ_I[c]	$\Delta E°'$,[d] mV	$\Delta\nu_{CO}{}^{A_1}$,[e] cm^{-1}	$\Delta\nu_{CO}{}^{E}$,[e] cm^{-1}	$10^5\Delta K_{CO}$,[e] dyn cm^{-1}	$\Delta\delta_{CO}$,[f] ppm	d_{Cr-C},[g] Å	d_{C-O},[g] Å	Δd,[g] Å
NEt_2	40.77	−20.40	4.15	−12.32	−16.47	0.10	−295	−20	−30	−0.41	1.74	1.813	1.159	0.155
NMe_2	41.01	−18.98	3.67	−11.01	−14.68	0.10	−300	−18	−26	−0.36	1.52			
NH_2	41.94	−17.58	3.94	−12.19	−16.13	0.10	−288	−12	−17	−0.23	1.97	1.825	1.152	0.133
OMe	49.00	−14.87	2.33	−7.71	−10.04	0.25	−94	−1	−3	−0.03	0.25	1.827	1.150	0.038
F	51.67	−13.50	2.94	−5.73	−6.67	0.52	78	8	9	0.14	−1.02			
Cl	18.22	−1.56	0.82	−3.81	−4.63	0.47	110	12	14	0.21	−1.15			
Me	16.56	1.47	−0.36	−3.3	−2.94	−0.05	−31	−5	−5	−0.07	0.29	1.824	1.151	0.027
$SiMe_3$	5.93	6.21	−2.12	−2.54	4.66	−0.12	10	−6	−4	−0.07	0.16	1.840	1.156	0.015
CO_2Me	−4.10	0.89	−2.68	2.31	4.99	0.30	150	11	17	0.24	−2.02	1.842	1.155	−0.004
CF_3	1.01	−2.98	−3.72	1.79	5.51	0.41	208	16	24	0.34	−2.57			

[a] $\Delta = \delta(\eta^6\text{-}C_6H_5X)Cr(CO)_3 - \delta(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (($CD_3)_2SO$). [b] $\Delta\pi = \Delta_{para} - \Delta_{meta}$ (($CD_3)_2SO$). [c] Taft's inductive substituent constants for uncomplexed arenes; see ref 18f in text. [d] Defined in the text (CH_2Cl_2/[n-Bu_4N]PF_6/Pt electrode). [e] Defined in the text (CH_2Cl_2). [f] Defined in the text (($CD_3)_2SO$). [g] Defined in the text; values calculated in ref 1b.

during the course of these studies was that the chemical reversibility of these oxidations (i.e. eq 7) could be dramatically increased (by up to 1 order of magnitude) by drying the CH_2Cl_2 and carrying out the electrochemical experiments in the presence of activated alumina.[22] The origin of this effect is unclear,[23,24] but it is certainly desirable since the presence of the alumina has no measurable adverse effects on the electrochemical parameters of interest for these complexes. In the following discussions, we will use the formal oxidation potentials, $E°'$, of the chemically reversible oxidations (0.390–1.160 V vs SCE) as our primary empirical measure of electron richness for the complexes (Table I).

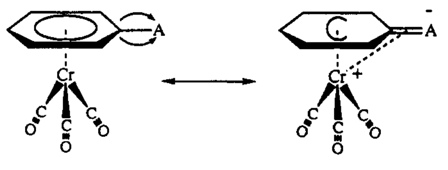
Discussion

Because the frontier orbitals on the substituents and the frontier orbitals of the matching symmetries on the (η^6-aryl)Cr(CO)$_3$ fragments interact, any substituents added to the benzene ring would be expected to modify the highest occupied molecular orbital, HOMO, wave functions and energies.[8z,9a,g,i,x,25] Qualitatively, the addition to the arene of substituents more electronegative than H (e.g. NEt_2, NMe_2, NH_2, OMe, F, Cl, CF_3, C(O)Me, CO_2Me) would be expected to make the metal centers in the complexes relatively electron poor by the inductive withdrawal of electron density. Similarly, substituents which are less electronegative than H (e.g. Me, $SiMe_3$) would be expected to inductively transfer electron density to the Cr(CO)$_3$ center. However, these substituents are also capable of π-symmetry interactions with the complex.[9a,g,i,x] Thus, π-donor substituents (e.g. NEt_2, NMe_2, NH_2, OMe, F, Cl, Me) would be expected to increase the electron transfer to Cr(CO)$_3$ and this can be represented, in valence bond terms, as an increased contribution from a zwitterionic resonance form having a negative charge localized on chromium and a positive charge on the π-donor substituent, i.e.



3a 3b

(see eq 2).[1b] Similarly, π-acceptor substituents (e.g. $SiMe_3$, CO_2Me, C(O)Me, CF_3) would be expected to decrease the electron richness of the metal center due to an increased delocalization of electron density onto the π-acceptor substituents and thus an increased contribution from the zwitterionic resonance form having a positive charge localized on chromium, i.e.



4a 4b

(see eq 3).[1b] Thus, for many substituents (e.g. NR_2, OMe,

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(18) The ^{13}C NMR spectra of uncomplexed arenes are also often assigned with the aid of the characteristic substituent constants of the arene substituents; see, for example: (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; John Wiley and Sons: New York, 1980. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; John Wiley and Sons: New York, 1982. (d) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089–3094. (e) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499–524. (f) Katritzky, A. R.; Topsom, R. D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 87–100. (g) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229–342. (h) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429–2440. (i) Hugel, H. M.; Kelly, D. P.; Spear, R. J.; Bromilow, J.; Brownlee, R. T. C.; Craik, D. J. *Aust. J. Chem.* **1979**, *32*, 1511–1519. (j) Brownlee, R. T. C.; Sadek, M. *Aust. J. Chem.* **1981**, *34*, 1593–1602. (k) Bromilow, J.; Brownlee, R. T. C.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 2020–2022. (l) Maciel, G. E.; Natterstad, J. J. *J. Chem. Phys.* **1965**, *42*, 2427–2435.

(19) For a discussion of the various Taft, Hammett, etc. substituent parameters, see, for example: (a) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1985; pp 202–215, 442–473. (b) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; pp 1–69. (c) Hind, J. *Physical Organic Chemistry* McGraw-Hill: New York, 1962; pp 81–103.

(20) The chemical shifts of the carbonyl carbons in these complexes increases (i.e. the CO ligands are deshielded) with increasing electron richness on the metal center. This is presumably due to the dominance of the paramagnetic term in the chemical shift tensor. See, for example: (a) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406–3412. (b) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* **1977**, *16*, 2497–2500.

(21) These radical cations are known to decompose under these conditions by an ECE mechanism involving associative nucleophilic attack on the radical cation.[8c] The rate of these processes is dependent upon both cell conditions (e.g. temperature, solvent, support electrolyte, trace impurity identity and concentration), which were maintained relatively constant throughout our studies, and the identity of the arene, which was systematically varied.[4b,c,8]

(22) We have tried many different aluminas, including those activated for extended periods under heat and vacuum. The best results were obtained when a particular alumina from ICN Biomedical (neutral, W200 Super-I) was used without further activation.

(23) It is most likely to arise either by super drying the solvent or, more likely, by the removal of trace impurities from the solvent/cell system.

(24) This observation has been independently confirmed: W. E. Geiger, Department of Chemistry, University of Vermont, personal communication.

(25) The substituents on uncomplexed arenes are also known to strongly influence HOMO and LUMO energies; see ref 8z and: (a) Dillow, G. W.; Kebarle, P. *J. Am. Chem. Soc.* **1989**, *111*, 5592–5596. (b) Chowdhury, S.; Kishi, H.; Dillow, G. W.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 603–610. (c) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301. (d) Neikam, W. C.; Desmond, M. M. *J. Am. Chem. Soc.* **1964**, *86*, 4811–4814. (e) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916–918. (f) Turner, D. W. *Adv. Phys. Org. Chem.* **1966**, *4*, 31–71 and references cited therein.

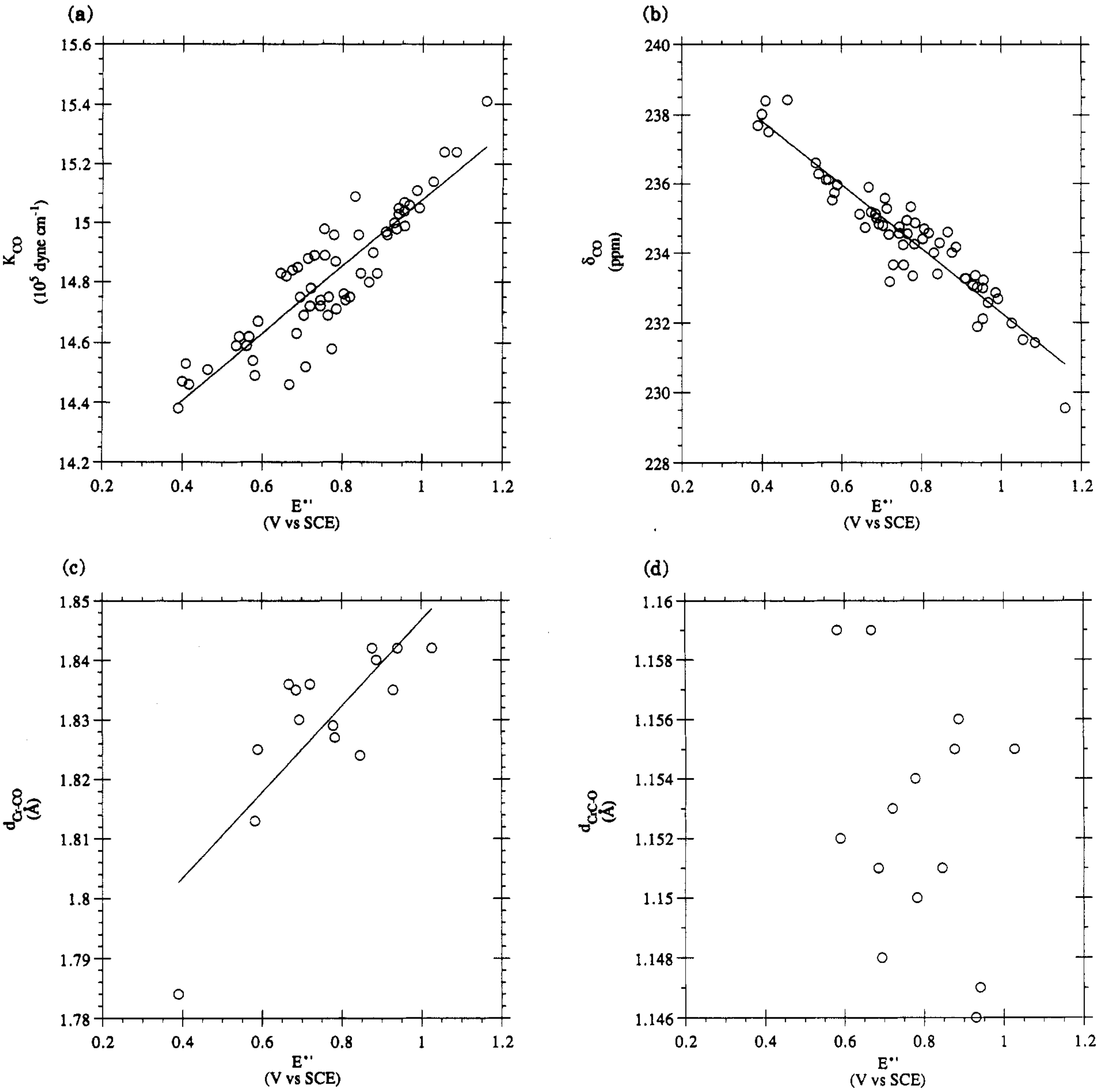

Figure 1. IR carbonyl stretching force constant, K_{CO} (a), ^{13}C NMR carbonyl chemical shifts, δ_{CO} (b), and carbonyl bond lengths, d_{Cr-CO} (c) and d_{CrC-O} (d), as a function of formal oxidation potentials, $E^{\circ\prime}$, in (η^6-arene)Cr(CO)$_3$ complexes.

F, Cl, SiMe$_3$) the inductive and π-donor/π-acceptor interactions would be expected to have opposite effects on the electron richness of the complexes, while for others (e.g. Me, CO$_2$Me, C(O)Me, CF$_3$) these effects would be expected to be mutually reinforcing. Our crystallographic results[1b] suggested to us that the π-donor and π-acceptor interactions might be particularly important for many substituents in determining the complexes' net electron richness when substituents were added to the arene. To test this hypothesis, we therefore sought methods of measuring the electron richness of the chromium centers (i.e. HOMO energies). Although ionization potential, IP, or photoelectron spectroscopy, PES, data would be ideal for this purpose, they are not available for (η^6-arene)Cr(CO)$_3$ complexes having a sufficiently wide range of substituted arenes.[8a,9c,e,t] However, less direct measures of the electron richness of the 63 (η^6-arene)Cr(CO)$_3$ complexes used in this study are available from at least four independent techniques (carbonyl stretching frequencies/force constants from IR spectra, ^{13}C NMR chemical shifts for the carbonyl carbon atoms, Cr–CO and CrC–O bond lengths from X-ray crystal structure studies, and oxidation potential data for the complexes from cyclic voltammetry studies) and these were expected to be useful for evaluating our model.[26]

Inspection of the relevant ν_{CO}, K_{CO}, δ_{CO}, $E^{\circ\prime}$, Cr–CO, and CrC–O data recorded in Table I for each of the 63 (η^6-arene)Cr(CO)$_3$ complexes that we have prepared indicates that, as expected, these varied measures of electron richness are in qualitative agreement. Thus, electron-rich complexes have low carbonyl stretching frequencies and force constants, high ^{13}C NMR chemical shifts for their carbonyl ligands,[20] low formal oxidation potentials, long CrC–O bonds, and short Cr–CO bonds.[1b] In contrast, the electron-poor complexes display the opposite trends. A more quantitative presentation of this data is given in Figure 1, where k_{CO}, δ_{CO}, d_{CrC-O} and d_{Cr-CO} are plotted as

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(26) Although individual studies using each of these techniques have been reported,[5-8,11] each study has generally dealt only with a relatively limited series of complexes (generally, only with monosubstituted arenes or arenes with only alkyl substituents) and this work is highly fragmented since each research group has generally studied different series of complexes by different techniques (e.g. IR, ^{13}C NMR, or cyclic voltammetry) and under different conditions (e.g. solvent, temperature, support electrolyte, etc.). The results of these studies are therefore often difficult to compare to one another in a quantitative fashion.

Table III. Results of Linear Least-Squares Regression Analyses for the Data ($y = mx + b$)[a]

dependent var[b] y	independent var[b] x	slope m	intercept b	corr coeff R
$\Delta\nu^{1/2}$	$E^{\circ\prime}$(V)	−1.00 (V^{-1})	3.2	0.67
$\Delta\nu^{1/2}$	δ_{CO} (ppm)	0.06 (ppm^{-1})	−12	0.48
$\Delta\nu^{1/2}$	K_{CO} (10^5 dyn cm^{-1})	−0.4 (10^{-5} dyn^{-1} cm)	9	0.39
$\Delta\nu^{1/2}$	K_{CO}^{i} (10^5 dyn cm^{-1})	3 (10^{-5} dyn^{-1} cm)	1	0.31
$\Delta\nu^{1/2}$	$\sum\Delta_\pi$ (ppm)	−0.013 (ppm^{-1})	2.3	0.54
$\Delta\nu^{1/2}$	$\sum\sigma_I$	−0.04	2	0.04
K_{CO} (10^5 dyn cm^{-1})	**$E^{\circ\prime}$ (V)**	**1.12 (10^5 V^{-1} dyn cm^{-1})**	**14.0 (10^5 dyn cm^{-1}**	**0.89**
δ_{CO} (ppm)	**$E^{\circ\prime}$ (V)**	**−9.21 (V^{-1} ppm^{-1})**	**241.5 (ppm)**	**0.94**
d_{Cr-CO} (Å)	**$E^{\circ\prime}$ (V)**	**0.072 (Å V^{-1})**	**1.77 (Å)**	**0.80**
d_{CrC-O} (Å)	**$E^{\circ\prime}$ (V)**	**−0.009 (Å V^{-1})**	**1.2 (Å)**	**0.30**
K_{CO}^{i} (10^5 dyn cm^{-1})	$E^{\circ\prime}$ (V)	−0.11 (10^{-5} V^{-1} dyn cm^{-1})	0.51 (10^5 dyn cm^{-1})	0.85
$\nu_{CO}^{A_1} - \nu_{CO}^{E}$ (cm^{-1})	$E^{\circ\prime}$ (V)	−25 (V^{-1} cm^{-1})	100 (cm^{-1})	0.86
$\nu_{CO}^{A_1}$ (cm^{-1})	$E^{\circ\prime}$ (V)	56 (V^{-1} cm^{-1})	1930 (cm^{-1})	0.88
ν_{CO}^{E} (cm^{-1})	$E^{\circ\prime}$ (V)	81 (V^{-1} cm^{-1})	1830 (cm^{-1})	0.89
δ_{CO} (ppm)	K_{CO} (10^5 dyn cm^{-1})	−7.37 (10^{-5} ppm^{-1} dyn cm^{-1})	343.6 (ppm)	0.94
K_{CO}^{i} (10^5 dyn cm^{-1})	K_{CO} (10^5 dyn cm^{-1})	−0.110	2.05 (10^5 dyn cm^{-1})	0.93
$\nu_{CO}^{A_1} - \nu_{CO}^{E}$ (cm^{-1})	K_{CO} (10^5 dyn cm^{-1})	−24 (10^{-5} dyn^{-1})	440 (cm^{-1})	0.95
d_{Cr-CO} (Å)	K_{CO} (10^5 dyn cm^{-1})	0.048 (Å V^{-1})	1.1 (Å)	0.76
d_{CrC-O} (Å)	K_{CO} (10^5 dyn cm^{-1})	−0.014 (Å V^{-1})	1.4 (Å)	0.67
Δd (Å)	**$\Delta E^{\circ\prime}$ (V)**	**−0.38 (Å mV^{-1})**	**0.022 (Å)**	**0.95**
Δd (Å)	ΔK_{CO} (10^5 dyn cm^{-1})	−0.29 (10^{-5} Å dyn^{-1} cm)	0.029 (Å)	0.89
Δd (Å)	$\Delta\delta_{CO}$ (ppm)	0.042 (Å ppm^{-1})	0.038 (Å)	0.85
Δd (Å)	Δd_{Cr-CO} (Å)	−5.0	9.1 (Å)	0.81
Δd (Å)	Δd_{CrC-O} (Å)	6	−7 (Å)	0.32
$E^{\circ\prime}$ (V)	**$\sum\Delta_\pi$ (ppm)**	**0.015 (V ppm^{-1})**	**0.96 (V)**	**0.86**
$E^{\circ\prime}$ (V)	**$\sum\sigma_I$**	**0.2 (V)**	**0.7 (V)**	**0.25**
K_{CO} (10^5 dyn cm^{-1})	$\sum\Delta_\pi$ (ppm)	0.018 (10^5 ppm^{-1} dyn cm^{-1})	15.0 (10^5 dyn cm^{-1})	0.77
K_{CO} (10^5 dyn cm^{-1})	$\sum\sigma_I$	0.49 (10^5 dyn cm^{-1})	15.0 (10^5 dyn cm^{-1})	0.58
δ_{CO} (ppm)	$\sum\Delta_\pi$ (ppm)	−0.15	232.4 (ppm)	0.83
δ_{CO} (ppm)	$\sum\sigma_I$	−3.1 (ppm)	235 (ppm)	0.47
d_{Cr-CO} (Å)	$\sum\Delta_\pi$ (ppm)	0.000 83 (Å ppm^{-1})	1.84 (Å)	0.55
d_{Cr-CO} (Å)	$\sum\sigma_I$	0.001 (Å ppm^{-1})	1.83 (Å)	0.12
d_{CrC-O} (Å)	$\sum\Delta_\pi$ (ppm)	0.0002 (Å ppm^{-1})	1.15 (Å)	0.27
d_{CrC-O} (Å)	$\sum\sigma_I$	−0.011 (Å ppm^{-1})	1.16 (Å)	0.52
$E^{\circ\prime}$ (V)	**no. of Me**	**−0.033 (V)**	**0.88 (V)**	**0.98**
K_{CO} (10^5 dyn cm^{-1})	no. of Me	−0.076 (10^5 dyn cm^{-1})	14.9 (10^5 dyn cm^{-1})	0.99
δ_{CO} (ppm)	no. of Me	0.34 (ppm)	234 (ppm)	0.99
$E^{\circ\prime}$ (V)	**no. of OMe**	**−0.064 (V)**	**0.86 (V)**	**0.98**
$E^{Me}{}_{1,3}$ (V)	**$E^{\circ\prime}$ (V)**	**−0.01**	**−0.01 (V)**	**0.28**
$E^{OMe}{}_{1,3}$ (V)	**$E^{\circ\prime}$ (V)**	**0.15**	**−0.2 (V)**	**0.38**
$E^{NH2}{}_{1,3}$ (V)	**$E^{\circ\prime}$ (V)**	**0.24**	**−0.46 (V)**	**0.68**
$E^{CO_2Me}{}_{1,3}$ (V)	**$E^{\circ\prime}$ (V)**	**0.14**	**0.026 (V)**	**0.93**
$E^{Me}{}_{1,4}$ (V)	$E^{\circ\prime}$ (V)	−0.01	−0.03 (V)	0.18
$E^{OMe}{}_{1,4}$ (V)	$E^{\circ\prime}$ (V)	−0.094	−0.0093 (V)	0.75
$E^{NH2}{}_{1,4}$ (V)	$E^{\circ\prime}$ (V)	−0.29	−0.024 (V)	0.92
$E^{NMe_2}{}_{1,4}$ (V)	$E^{\circ\prime}$ (V)	−0.29	−0.022 (V)	−0.97
$E^{CO_2Me}{}_{1'4}$ (V)	$E^{\circ\prime}$ (V)	−0.02	0.2 (V)	0.18
$i_{p,c}/i_{p,a}$	**$E^{\circ\prime}$ (V)**	**−0.32 (V^{-1})**	**1.1**	**0.60**
$i_{p,c}/i_{p,a}$	K_{CO} (10^5 dyn cm^{-1})	−0.28 (10^{-5} dyn^{-1} cm)	5.0	0.67
$i_{p,c}/i_{p,a}$	δ_{CO} (ppm)	0.034 (ppm^{-1})	−7.0	0.62
$i_{p,c}/i_{p,a}$	$\sum\Delta_\pi$ (ppm)	−0.003 (ppm^{-1})	0.8	0.37
$i_{p,c}/i_{p,a}$	$\sum\sigma_I$	−0.18	0.9	0.55

[a] These analyses were carried out using the program KaleidaGraph by Synergy Software. The K_{CO} and K_{CO}^{i} values used are 10^{-5} times the actual values. Values in bold face are plotted in Figures 1–6. [b] The variables are defined in the text.

a function of $E^{\circ\prime}$, and in Table III, in which the results of a linear least-squares regression analysis of the relationships between these sets of data are presented. It is interesting to note that, although each of these scales actually measures a very different physical phenomenon, reasonably good correlations between these different parameters are observed (for k_{CO} and $E^{\circ\prime}$, $R = 0.89$, for δ_{CO} and $E^{\circ\prime}$, $R = 0.94$, and for d_{Cr-CO} and $E^{\circ\prime}$, $R = 0.80$). This provides strong evidence for the validity of our use of one scale, $E^{\circ\prime}$, as our primary measure of electron richness for most of the latter data evaluation. It also suggests that the HOMO of the complex (from which oxidation removes the electron) has a substantial component of its electron density on the $Cr(CO)_3$ center, since this is where the other techniques detect changes in electron density. The poorest correlations are observed for the bond-length data of the carbonyl ligands, which are known to be relatively insensitive to the degree of back-bonding (particularly the CrC–O bond lengths).[27] Given the correlations between these various empirical scales of electron richness, and since $E^{\circ\prime}$ is very precisely measured and is the parameter most directly related to HOMO energy, the formal oxidation potentials will be used as our primary measure of the electron richness of the complexes. However, the parameters derived from the IR and ^{13}C NMR data (i.e. k_{CO}, δ_{CO}) generally give analogous statistical results (Table III and the supplementary material).

Comparison of the data for the monosubstituted complexes, $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$, to that for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ also allows us to establish the incremental effect of each substituent X upon these parameters (i.e. $\Delta E^{\circ\prime}$, $\Delta\nu_{CO}^{A_1}$, $\Delta\nu_{CO}^{E}$, ΔK_{CO}, $\Delta\delta_{CO}$, Δ_{Cr-C}, Δ_{C-O}). These values are presented in Table II along with various other substituent parameters (i.e. Δd,[28] Δ_π, σ_I,[19]). It is interesting to note that the

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(27) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing: Monterey, CA, 1985; pp 36–38.

(28) The parameter Δd is a measure of the structural distortion of the arene ring in the complexes away from planarity.[1b]

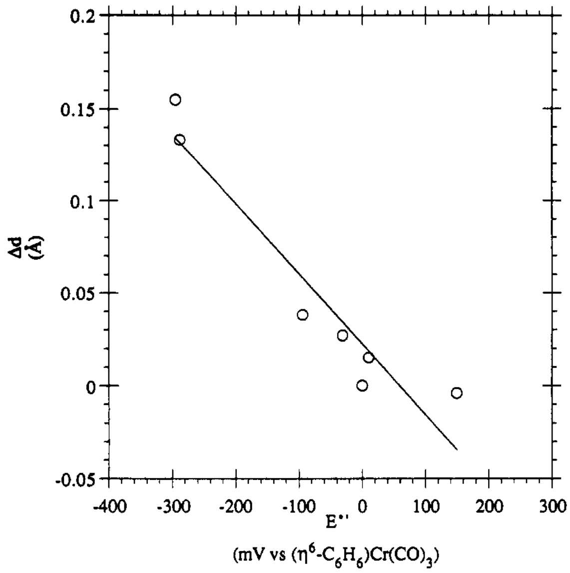

Figure 2. Structural distortion, Δd, as a function of the formal oxidation potentials, $E^{\circ\prime}$, in (η^6-C$_6$H$_5$X)Cr(CO)$_3$ complexes.

magnitude and sign of the structural distortion parameter, Δd,[1b] is dependent upon the electron richness of the metal center (Figure 2, Table III; e.g. $R = 0.95$ for Δd vs E°′), and this allows one to predicts some aspects of the X-ray structure from electrochemical, IR, or ^{13}C NMR data, as our model predicts![1b] This same model also predicts that the electron richness of the complexes (as measured by $E^{\circ\prime}$, K_{CO}, δ_{CO}, $d_{\text{Cr-CO}}$, $d_{\text{CrC-O}}$, etc.) should also be dependent on substituent π-donor/π-acceptor character. Using the data in Table I, we can now test this prediction. In Figure 3, $E^{\circ\prime}$ is plotted as a function of both total $\Delta\pi$ ($\sum\Delta_\pi$, as a representative measure of π-donor/π-acceptor resonance character)[1b] and total σ_{I} ($\sum\sigma_{\text{I}}$, as a representative measure of inductive character).[19] As we expected, the degree of inductive electron donation or electron withdrawal is a very poor predictor of the total electron richness of the Cr(CO)$_3$ center as measured by $E^{\circ\prime}$, K_{CO}, δ_{CO} $d_{\text{Cr-CO}}$ and $d_{\text{CrC-O}}$ (Table III; e.g. $R = 0.25$ for $E^{\circ\prime}$ vs $\sum\sigma_{\text{I}}$). One reason for this is that many of the substituents which are the most strongly σ-electron withdrawing (e.g. F, NR$_2$, OMe) are also strongly π-donating, while some σ-donating groups (e.g. SiMe$_3$) are weakly π-accepting. Indeed, the data in Figure 3 clearly show that substituent π-donor/π-acceptor character is the dominant factor in determining the electron richness of each complex when arene substituents having a broad range of π-donor and π-acceptor characters are used (i.e. $R = 0.86$ for $E^{\circ\prime}$ vs $\sum\Delta_\pi$). In contrast, it appears that inductive effects play a dominant role in determining the electron richness of the complexes only when the substituents are *not* strongly π-donating or π-accepting (e.g. for alkyl substituents).[29] Interestingly, the data listed in Table III for the dependence of $E^{\circ\prime}$, K_{CO}, and δ_{CO} on $\sum\Delta_\pi$ and $\sum\sigma_{\text{I}}$ indicate that the K_{CO} values show the largest dependence on inductive effects and the smallest dependence on π-donor/π-acceptor effects, while $E^{\circ\prime}$ shows the smallest dependence on inductive effects and the largest dependence of π-donor/π-acceptor effects. This result is quite surprising, but a detailed explanation must await a thorough theoretical study.

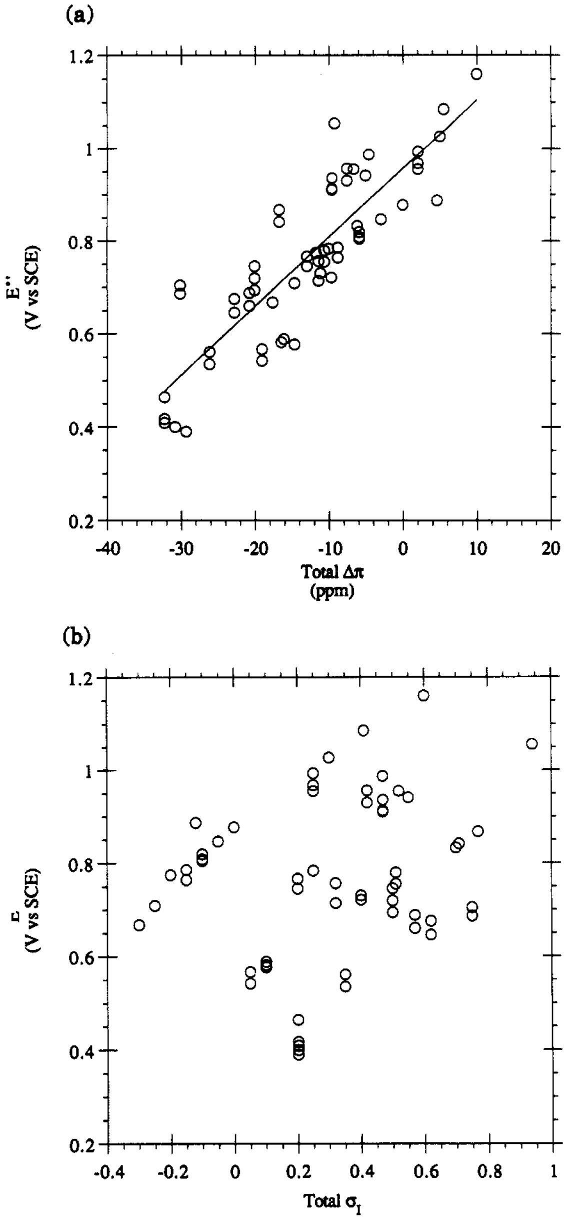

Figure 3. Formal oxidation potentials, $E^{\circ\prime}$, as a function of (a) the total π-donor/π-acceptor parameter, $\Delta\pi$, and (b) the total inductive parameter, σ_{I}, in (η^6-arene)Cr(CO)$_3$ complexes.

Cyclic voltammetric studies on the methyl-substituted (η^6-C$_6$H$_{6-n}$Me$_n$)Cr(CO)$_3$ complexes (where $n = 1$–6) have shown,[8h,ij,z] and we have independently confirmed (see Table I), that the effects of adding methyl substituents to an (η^6-arene)Cr(CO)$_3$ complex are approximately linearly additive, that no electronic saturation of the metal's ability to accept electron density occurs (i.e. the incremental effect on the oxidation potential of the complex of adding the sixth methyl group is approximately the same as that for adding the first), and that the substitution geometry about the arene ring has only a small effect on the oxidation potential in these species. This linear relationship is illustrated in Figure 4a, where our oxidation potential data for the methyl-substituted (η^6-arene)Cr(CO)$_3$ complexes is plotted as a function of the number of methyl substituents. However, this linear additivity of the incremental substituent effects of the methyl groups is somewhat counter intuitive, since one would expect that the metals' ability to accept or donate electron density would be saturated at some point. More consistent with intuition,

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(29) The methyl group is a weak, but significant, π-donor (i.e. $\Delta_\pi = -2.94$ ppm); see: (a) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370–1383. (b) Calhorda, M. J.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Galvao, A. M.; Garcia, M. H.; Martins, A. M.; Minas, da Piedade, M. E.; Pinheiro, C. I.; Romao, C. G.; Martinho Simoes, J. A.; Veiros, L. F. *Organometallics* **1991**, *10*, 483–494.

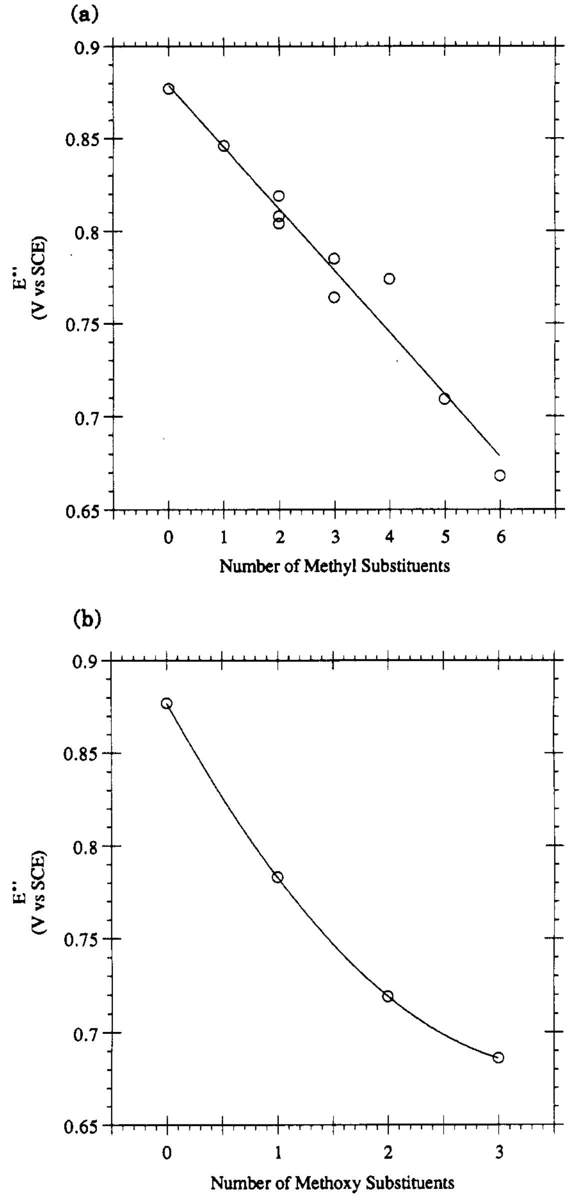


Figure 4. Formal oxidation potentials, $E^{\circ\prime}$, as a function of the number of (a) Me and (b) OMe substituents on the arene ring, in (η^6-arene)$Cr(CO)_3$ complexes.

the data for substituents more strongly π-electron donating than is Me[29] clearly indicates that such electronic saturation does occur (e.g. Figure 4b) and that the addition of each further electron-donating substituent is observed to have a smaller incremental effect on the oxidation potential than the previous one.[30] Similarly, one would expect that the incremental effect on the oxidation potential of a complex of adding an electron-donating or electron-accepting substituent, Y, to a monosubstituted complex to give a meta-disubstituted complex (i.e. (η^6-1,3-C_6H_4YX)$Cr(CO)_3$) would depend on the electron richness of the initial complex (i.e. (η^6-C_6H_5X)$Cr(CO)_3$). This incremental effect of adding a substituent Y to the complex, $\Delta E^{Y}_{1,3}$, is defined as

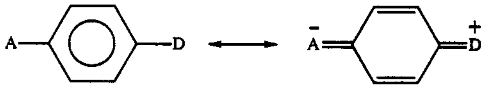
$$\Delta E^{Y}_{1,3} = E^{\circ\prime}((\eta^6\text{-}1,3\text{-}C_6H_4YX)Cr(CO)_3) - E^{\circ\prime}((\eta^6\text{-}C_6H_5X)Cr(CO)_3) \quad (8)$$

and, in Figure 5, $\Delta E^{Y}_{1,3}$ is plotted as a function of the formal oxidation potential of the initial complex (η^6-C_6H_5X)$Cr(CO)_3$) for Y = Me, OMe, NH_2, and CO_2Me. For the weakly π-donating methyl substituent (i.e. where Δ_π = −2.94 ppm),[29] there is no dependence of incremental oxidation potential on the electron richness of (η^6-C_6H_5X)$Cr(CO)_3$ (Figure 5a). However, for the more strongly π-donating or π-accepting NH_2, OMe, and CO_2Me groups (i.e. where Δ_π = −16.13, −10.04, and 4.99 ppm, respectively) their incremental effects on the oxidation potentials are more dependent upon the electron richness of the starting complexes (Figure 5b–d). Analogous trends in the dependence of $\Delta E^{Y}_{1,4}$, i.e.

$$\Delta E^{Y}_{1,4} = E^{\circ\prime}((\eta^6\text{-}1,4\text{-}C_6H_4YX)Cr(CO)_3) - E^{\circ\prime}((\eta^6\text{-}C_6H_5X)Cr(CO)_3) \quad (9)$$

on the nature of Y are seen for the para-substituted complexes as well (i.e. where Y = OMe, NH_2, and NMe_2; Table III).

For uncomplexed arenes, it is well established that π-symmetry resonance interactions are much stronger for para substituents than they are for meta substituents, e.g.



5a 5b

and this difference has been exploited to optimize the properties of such species for a wide variety of practical applications.[31] One would therefore predict that, in (η^6-arene)$Cr(CO)_3$ complexes, there would also be stronger π-symmetry resonance interactions for para substituents than for meta substituents and that this might cause differences in the electron richness of isomeric (η^6-arene)$Cr(CO)_3$ complexes. Small differences of this type have been measured experimentally for uncomplexed arenes[8z,25c–f] and for methyl-substituted (η^6-arene)$Cr(CO)_3$ complexes.[8h,i,j,z] However, one would expect that more strongly π-donating and π-accepting substituents would produce larger differences in the electron richness of substituted (η^6-arene)$Cr(CO)_3$ complexes and this might be detectable experimentally. Inspection of the data in Table I for pairs of isomeric complexes indicates that, although no significant differences are observed in the IR- and ^{13}C NMR-based measures of electron richness, there are significant differences observed between the electron richness of isomeric *meta-* and *para-substituted* complexes as measured by cyclic voltammetry. Thus, for every pair of isomeric (η^6-$C_6H_4D_2$)$Cr(CO)_3$ complexes (where D is a π-donor), the para-substituted complex is more electron rich and therefore more readily oxidized than is the meta-substituted complex. Indeed, the average magnitude of this difference for 11 pairs of isomeric complexes, i.e.

$$E^{\circ\prime}_{1,4} - E^{\circ\prime}_{1,3} = -23 \pm 6 \text{ mV} \quad (10)$$

is similar to the incremental effect of adding a methyl substituent to a complex (for Me, $\Delta E^{\circ\prime}$ = −33 mV). Interestingly, even for the dimethyl complexes (i.e. (η^6-$C_6H_4Me_2$)$Cr(CO)_3$) having the weakly π-donating methyl

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(30) For example, the addition of the first electron-donating OMe substituent to (η^6-C_6H_6)$Cr(CO)_3$ causes $E^{\circ\prime}$ to decrease by 94 mV, the addition of the second OMe substituent to (η^6-$C_6H_5(OMe)$)$Cr(CO)_3$ causes $E^{\circ\prime}$ to decrease by a further 64 mV, but the addition of the third OMe group to the C5 carbon of (η^6-1,3-$C_6H_4(OMe)_2$)$Cr(CO)_3$ causes $E^{\circ\prime}$ to decrease by only 33 mV. For the even more strongly electron-donating NH_2 substituent, this saturation effect is further exaggerated with the first and second incremental changes in $E^{\circ\prime}$ being 288 and 172 mV, respectively. A smaller saturation effect is observed for the π-accepting CO_2Me substituent. Thus, the first and second incremental changes in $E^{\circ\prime}$ are 150 and 133 mV, respectively.

(31) See, for example: Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991; pp 134–143.

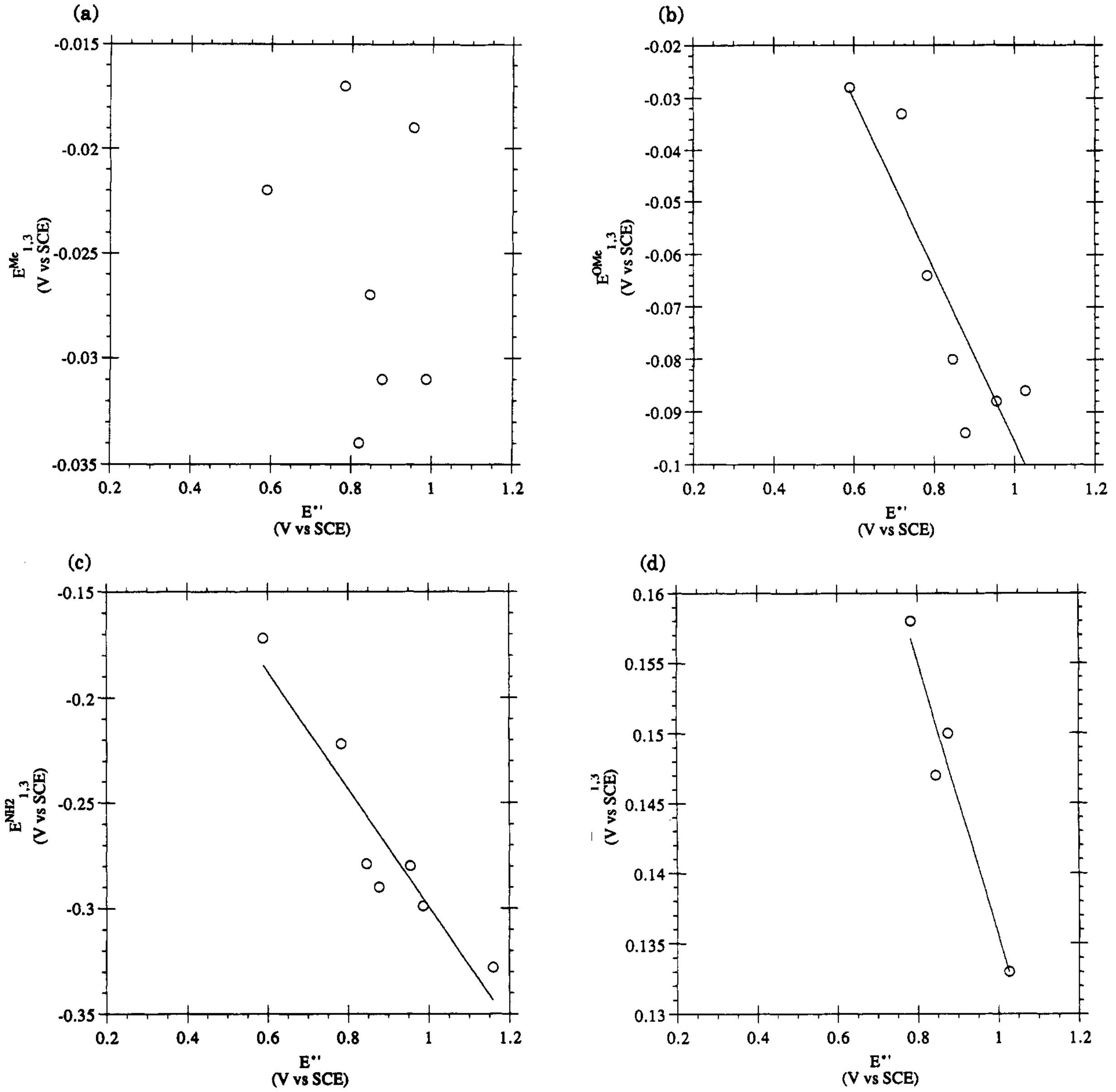

Figure 5. Incremental effects of meta substituents on the oxidation potentials of the (η^6-arene)Cr(CO)$_3$ complexes, $E^{Y}_{1,3}$, as a function of the electron richness of the complexes, $E^{\circ\prime}$ for (a) Y = Me, (b) Y = OMe, (c) Y = NH$_2$, and (d) Y = CO$_2$Me, in (η^6-arene)Cr(CO)$_3$ complexes.

group,[29] the para-substituted complex is significantly more electron rich ($E^{\circ\prime}_{1,4} - E^{\circ\prime}_{1,3} = -14$ mV,[8h,i,j] and -15 mV (this work)) than is the meta-substituted complex as it is for the uncomplexed arene[8z,25c-f] and our organometallic derivatives (i.e. (η^6-C$_6$H$_4$Fp$_2$)Cr(CO)$_3$).[3a,4] For the three pairs of isomeric (η^6-C$_6$H$_4$(NH$_2$)A)Cr(CO)$_3$ complexes (i.e. where NH$_2$ is a strong π-donor and A is the π-acceptor substituents C(O)Me, CO$_2$Me, and CF$_3$), the para-substituted complex is more electron poor, and therefore more difficult to oxidize, than is the meta-substituted complex, i.e.[32]

$$E^{\circ\prime}_{1,4} - E^{\circ\prime}_{1,3} = 43 \pm 16 \text{ mV} \qquad (11)$$

These differences in oxidation potentials between pairs of isomers are difficult to adequately explain in valence bond or elementary molecular orbital terms. Indeed, a satisfactory explanation must clearly await detailed molecular orbital calculations in which isomeric pairs of complexes are compared and in which the role of arene geometry (which is very nonplanar for these species)[1b] is explored.

The chief strategy reported in the literature to stabilize [(η^6-arene)Cr(CO)$_3$]$^{\bullet+}$ radical cations has been to place bulky substituent(s) on the arene ring.[8] Although there is some controversy about the importance of steric effects,[8h] it is widely reported that these complexes are stabilized by the steric bulk of the alkyl groups which protects the metal-centered radical cations (e.g. [(η^6-C$_6$Me$_6$)Cr(CO)$_3$]$^{\bullet+}$) from attack by incoming nucleophiles.[8g,n,o] However, we noticed during the course of our early studies that the oxidation potentials of the substituted (η^6-arene)Cr(CO)$_3$ complexes seemed to be an important predictive factor, at least in a qualitative sense, in the stabilization of the radical cations. Indeed, in the extreme, we observed that those complexes showing the lowest chemical reversibilities also had the most electron-poor metal centers and vice versa (Table I). For example, K_{CO} was greater than 15.25 × 10^5 dyn cm^{-1} for the three complexes whose oxidations were totally chemically irreversible at 100 mV s^{-1} and at ambient temperatures. More quantitatively, we see in Figure 6 and Table III that, for the (η^6-arene)Cr(CO)$_3$

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(32) Unfortunately, the (η^6-C$_6$H$_4$A$_2$)Cr(CO)$_3$ complexes were difficult to prepare[17] and were generally not oxidized in a chemically reversible manner at the scan rates employed in our study (up to 10 V s^{-1}). Therefore, the electron richness of these isomeric complexes cannot be tested at this time.

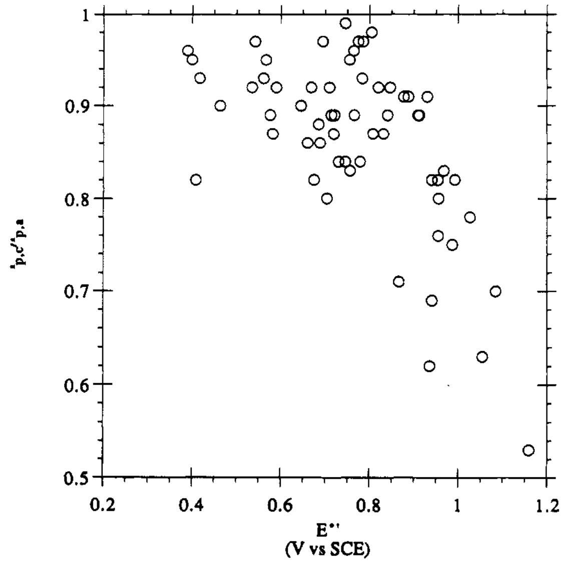

Figure 6. Chemical reversibility, $i_{p,c}/i_{p,a}$, as a function of formal oxidation potentials, $E°'$, for the complexes, in (η^6-arene)$Cr(CO)_3$ complexes.

complexes, the chemical reversibilities (as measured by $i_{p,c}/i_{p,a}$) appear to show some qualitative dependence upon the complexes' electron richness as measured by $E°'$, K_{CO}, and δ_{CO}. In retrospect, this is not unexpected, since electron transfer to the $Cr(CO)_3$ center from the substituents would partially delocalize the chromium-centered orbitals onto π-donor substituents and this would decrease the fractional positive charge on the chromium atom and would be expected to raise the energy of the half-empty HOMO of the radical cation. These effects would be expected to lower the electrophilicity of the radical cation and would therefore be expected to slow any nucleophilic attack which might lead to the radical cation's eventual decomposition.[21] In fact, it seems likely that the increased stability of sterically crowded complexes such as $[(\eta^6\text{-}C_6Me_6)Cr(CO)_3]^{\bullet +}$ (compared to $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]^{\bullet +}$) is *not* due primarily to steric protection by the alkyl substituents. Rather, the main cause of the increased stability which these bulky arenes provide is likely due, in most cases,[33] to the increased electron richness on the chromium center supplied by the six alkyl groups. Thus, it is not surprising that $[(\eta^6\text{-}C_6H_5(NH_2))Cr(CO)_3]^{\bullet +}$ ($E°' = 0.589$ mV) is approximately as kinetically stable toward decomposition as is $[(\eta^6\text{-}C_6Me_6)Cr(CO)_3]^{\bullet +}$ ($E°' = 0.709$ mV) even though the arene in the latter complex is much bulkier.

Conclusions

We have examined the electron richness of an extensive series of 63 substituted (η^6-arene)$Cr(CO)_3$ complexes. These studies have shown that π-symmetry resonance interactions between the substituents on the arene and the rest of the molecules are very important in understanding the electron richness of these species as measured by electrochemical, IR and ^{13}C NMR, and X-ray crystallographic data. In particular, we have clearly demonstrated that linear additivity in substituent effects *cannot* be safely assumed for other than the most weakly π-donating and π-accepting substituents, that saturation of the metal center's ability to accept electron density readily occurs, and that the stability of $[(\eta^6\text{-arene})Cr(CO)_3]^{\bullet +}$ radical cations appears to have a significant electronic component. These studies have also emphasized the close relationship among these varied measures of electron richness and suggest a number of important questions that deserve detailed theoretical analysis. We are currently extending these studies by investigating the reductive electrochemistry of these species and by relating these (η^6-arene)$Cr(CO)_3$ complexes having main-group substituents to their analogues having transition-metal-containing substituents.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for their support of this work. We also thank Jin Li, Lonni Shilliday, Dusan Ristic-Petrovic, Nadia Wichrowska, Kathy Mathews, and Cathy Chambers for their assistance in the synthesis and characterization of some of these complexes. We also thank Dr. G. Richter-Addo and Dr. T. Albright for helpful discussions and the donors to the Women in Scholarship Engineering Science and Technology program for their partial financial support for K. M. and C. C.

Registry No. $Cr(CO)_6$, 13007-92-6; 1,4-$C_6H_4(CO_2Me)_2$, 120-61-6; 1,4-$C_6H_4Cl_2$, 106-46-7; 1,4-$C_6H_4(NMe_2)_2$, 100-22-1; (η^6-C_6H_6)$Cr(CO)_3$, 12082-08-5; (η^6-$C_6H_5(NEt_2)$)$Cr(CO)_3$, 12242-29-4; (η^6-$C_6H_5(NMe_2)$)$Cr(CO)_3$, 12109-10-3; (η^6-$C_6H_5(NH_2)$)$Cr(CO)_3$, 12108-11-1; (η^6h$C_6H_5(OMe)$)$Cr(CO)_3$, 12116-44-8; (η^6-$C_6H_5(F)$)$Cr(CO)_3$, 12082-05-2; (η^6-$C_6H_5(Cl)$)$Cr(CO)_3$, 12082-03-0; (η^6-$C_6H_5(Me)$)$Cr(CO)_3$, 12083-24-8; (η^6-$C_6H_5(SiMe_3)$)$Cr(CO)_3$, 33248-13-4; (η^6-$C_6H_5(CO_2Me)$)$Cr(CO)_3$, 12125-87-0; (η^6-$C_6H_5(CF_3)$)$Cr(CO)_3$, 60429-40-5; (η^6-1,2-$C_6H_4(OMe_2)_2$)$Cr(CO)_3$, 12176-27-1; (η^6-1,2-$C_6H_4(NH_2)_2$)$Cr(CO)_3$, 55046-36-1; (η^6-1,2-$C_6H_4(F)(Me)$)$Cr(CO)_3$, 32913-59-0; (η^6-1,2-$C_6H_4(Me)_2$)$Cr(CO)_3$, 12129-29-2; (η^6-1,2-$C_6H_4(Me)(CO_2Me)$)$Cr(CO)_3$, 12214-93-6; (η^6-1,3-$C_6H_4(NH_2)_2$)$Cr(CO)_3$, 55046-37-2; (η^6-1,3-$C_6H_4(OMe)_2$)$Cr(CO)_3$, 12176-28-2; (η^6-1,3-$C_6H_4(Cl)_2$)$Cr(CO)_3$, 86409-61-2; (η^6-1,3-$C_6H_4(Me)_2$)$Cr(CO)_3$, 12129-28-1; (η^6-1,3-$C_6H_4(CO_2Me)_2$)$Cr(CO)_3$, 12242-11-4; (η^6-1,3-$C_6H_4(NH_2)(OMe)$)$Cr(CO)_3$, 36354-43-5; (η^6-1,3-$C_6H_4(NH_2)(F)$)$Cr(CO)_3$, 56237-50-4; (η^6-1,3-$C_6H_4(NH_2)(Me)$)$Cr(CO)_3$, 36352-77-9; (η^6-1,3-$C_6H_4(NH_2)(C(O)Me)$)$Cr(CO)_3$, 140873-99-0; (η^6-1,3-$C_6H_4(NH_2)(CF_3)$)$Cr(CO)_3$, 98357-76-7; (η^6-1,3-$C_6H_4(OMe)(F)$)$Cr(CO)_3$, 56213-62-8; (η^6-1,3-$C_6H_4(OMe)(Me)$)$Cr(CO)_3$, 12109-01-2; (η^6-1,3-$C_6H_4(OMe)(CO_2Me)$)$Cr(CO)_3$, 12153-80-9; (η^6-1,3-$C_6H_4(F)(Me)$)$Cr(CO)_3$, 33411-10-8; (η^6-1,3-$C_6H_4(Cl)(Me)$)$Cr(CO)_3$, 33411-11-9; (η^6-1,3-$C_6H_4(Me)(CO_2Me)$)$Cr(CO)_3$, 12214-94-7; (η^6-1,3-$C_6H_4(NH_2)(Cl)$)$Cr(CO)_3$, 36354-45-7; (η^6-1,4-$C_6H_4(NMe_2)_2$)$Cr(CO)_3$, 46930-56-7; (η^6-1,4-$C_6H_4(NH_2)_2$)$Cr(CO)_3$, 51733-34-7; (η^6-1,4-$C_6H_4(OMe)_2$)$Cr(CO)_3$, 12176-26-0; (η^6-1,4-$C_6H_4(Cl)_2$)$Cr(CO)_3$, 86409-62-3; (η^6-1,4-$C_6H_4(Me)_2$)$Cr(CO)_3$, 12129-27-0; (η^6-1,4-$C_6H_4(Co_2Me)_2$)$Cr(CO)_3$, 33039-20-2; (η^6-1,4-$C_6H_4(NMe_2)(NH_2)$)$Cr(CO)_3$, 140874-00-6; (η^6-1,4-$C_6H_4(NH_2)(OMe)$)$Cr(CO)_3$, 36354-44-6; (η^6-1,4-$C_6H_4(NH_2)(F)$)$Cr(CO)_3$, 36643-97-7; (η^6-1,4-$C_6H_4(NH_2)(Cl)$)$Cr(CO)_3$, 36354-46-8; (η^6-1,4-$C_6H_4(NMe_2)(CO_2Me)$)$Cr(CO)_3$, 63168-43-4; (η^6-1,4-$C_6H_4(Me)(CO_2Me)$)$Cr(CO)_3$, 12241-71-3; (η^6-1,4-$C_6H_4(NH_2)(Me)$)$Cr(CO)_3$, 12247-10-8; (η^6-1,4-$C_6H_4(NH_2)(C(O)Me)$)$Cr(CO)_3$, 36352-76-8; (η^6-1,4-$C_6H_4(NH_2)(CO_2Me)$)$Cr(CO)_3$, 12241-57-5; (η^6-1,4-$C_6H_4(NH_2)(CF_3)$)$Cr(CO)_3$, 98357-77-8; (η^6-1,4-$C_6H_4(OMe)(F)$)$Cr(CO)_3$, 56213-59-3; (η^6-1,4-$C_6H_4(OMe)(Me)$)$Cr(CO)_3$, 12109-02-3; (η^6-1,4-$C_6H_4(OMe)(CO_2Me)$)$Cr(CO)_3$, 12241-72-4; (η^6-1,4-$C_6H_4(F)(Me)$)$Cr(CO)_3$, 12116-25-5; (η^6-1,4-$C_6H_4(Cl)(Me)$)$Cr(CO)_3$, 12116-24-4; (η^6-1,3,5-$C_6H_3(OMe)_3$)$Cr(CO)_3$, 12193-70-3; (η^6-1,3,5-$C_6H_3(Me)_3$)$Cr(CO)_3$, 12129-67-8; (η^6-1,3,5-$C_6H_3(CO_2Me)_3$)$Cr(CO)_3$, 140874-01-7; (η^6-1,3,5-$C_6H_3(NH_2)(CO_2Me)_2$)$Cr(CO)_3$, 140874-02-8; (η^6-1,2,4-$C_6H_3(Me)_3$)$Cr(CO)_3$, 32913-41-0; (η^6-1,2,3-$C_6H_3(OMe)_3$)$Cr(CO)_3$, 12193-72-5; (η^6-1,2,4,5-$C_6H_2(Me)_4$)$Cr(CO)_3$, 33435-44-8; (η^6-$C_6H(Me)_5$)$Cr(CO)_3$, 32913-08-9; (η^6-$C_6(Me)_6$)$Cr(CO)_3$, 12088-11-8.

Supplementary Material Available: A table listing ^1H NMR data for the arenes and their substituents and ^{13}C NMR data for the arene substituents of the (η^6-arene)$Cr(CO)_3$ complexes and figures showing plots of the data from which are derived the least-squares regression analyses described in Table III (42 pages). Ordering information is given on any current masthead page.

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[33] However, the difference between the methyl complex and $[(\eta^6\text{-}C_6Et_6)Cr(CO)_3]^{\bullet +}$ is likely to be mostly steric, since the electronic properties of their substituents in the uncomplexed arenes are rather similar.[18e,19]