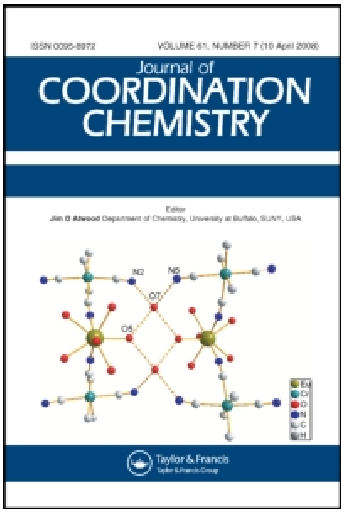

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EFFECTS OF MULTIPLE SUBSTITUENTS ON THE PHYSICAL PROPERTIES OF PENTACARBONYLARYLISOCYANIDECHROMIUM COMPOUNDS

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EFFECTS OF MULTIPLE SUBSTITUENTS ON THE PHYSICAL PROPERTIES OF PENTACARBONYLARYLISOCYANIDECHROMIUM COMPOUNDS

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Eight arylisocyanides containing one or more electron-withdrawing substituents were synthesized. The σ-donating and π-accepting abilities of these isocyanides were evaluated by examining the spectroscopic and electrochemical properties of the pentacarbonyl(isocyanide)chromium derivatives. Linear relationships between the Hammett parameters of the para-substituted isocyanides, ^{13}C NMR chemical shifts, and ν(CN) with the $E_{1/2}$ were found. Ortho substitutions of the isocyanide stabilized the HOMO of the $Cr(CO)_5L$ more than para substitutions. Furthermore, each successively added substituent caused a similar shift in the observed oxidation potential relative to its position on the isocyanide.

KEYWORDS: Arylisocyanides, chromium pentacarbonyl, Hammett correlations

INTRODUCTION

Arylisocyanide ligands have been used to vary the electron density on various metal centers.[1,2] These ligands allow systematic variation in the electronic properties and could allow variation in the steric properties of organometallic compounds. Such variations may be useful in the development of new catalytic systems. In order to utilize these ligands, an understanding of the effect of different substituents on the σ-donating and π-accepting abilities as well as steric properties must be developed. Previous work has demonstrated that substituents on the arylisocyanide ligand have a definite effect on the $E_{1/2}$ of the complex.[1,2] Treichel and Essenmacher found that $E_{1/2}$ can be correlated with Hammett parameters of the aryl substituents in hexaarylisocyanidechromium(0) and hexaarylisocyanidemanganese(I) compounds. Theoretical results support the observed effects on $E_{1/2}$.[3,4] All of these studies with chromium and manganese compounds indicate the $E_{1/2}$ is directly related to the energy of the HOMO. Furthermore, both inductive and resonance effects of the substituent must be important in determining the energy of the HOMO, since the Hammett parameter correlated linearly with $E_{1/2}$. Other theoretical studies have examined substituent effects on the isocyanide's orbitals that are involved in bonding to metals.[4,5] All of this work has yielded a better understanding of substituent's electronic effect on arylisocyanides.[4,6,7] However, no systematic work with ortho electron-withdrawing substituents has been reported. In order to use arylisocyanide ligands to control both electronic and steric properties at a metal center, the isocyanides will need to contain ortho substitutes or more substituents. In this work, we investigated the effects of multisubstituted arylisocyanides on the electronic and steric properties of metal complexes. We report the synthesis of eight substituted-arylisocyanides and the spectroscopic properties of thier corresponding pentacarbonyl(isocyanide)chromium compounds.

EXPERIMENTAL

Reagent grade chemicals were used without further purification. The substituted anilines and formic acid were obtained from Aldrich. The hexacarbonylchromium was obtained from Columbia Organics. All solvents were dried using standard procedures. Elemental analyses of vacuum-dried products were performed by Galbraith Laboratories (Knoxville, Tennessee). Infrared and NMR spectra were collected on Mattson Polaris and Varian VXR 300 instruments, respectively.

The cyclic voltammetic data were collected using an EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273 which is interfaced to, *via* an IEEE-488 bus, a 12 MHz PC-AT 286 clone computer (MMG computers). The software is from EG & G (model M270 version 3.0). Measurements were made at room temperature using a three compartment cell provided with a lugging probe which was placed a few millimeters from the working electrode. The working electrode was at Pt disk (10 micrometer disc). A Pt wire and Ag/AgCl (3M NaCl) were used as the auxiliary and reference electrodes, respectively. All the electrodes were obtained from Bioanalytical Systems. The voltammograms were collected with 95% IR compensation. Solutions of pentacarbonyl(isocyanide)chromium (3mM) and tetrabutylammonium tetrafluoroborate (0.1M) in acetonitrile were purged with argon and kept under an Ar blanket during the experiment. Sweep rates from 0.025 to 10 V/s were employed. At scan rates lower than 0.5 V/s a slow decomposition of the complexes took place which was clearly detected by an increase in the i_a/i_c values. Furthermore, at scans greater than 6 V/s all the complexes showed deviations in the i_a versus (sweep rate)$^{1/2}$ linear plots. A few complexes also showed a small deviation at scan rates slower than 6 V/s. A compromise between the slow decomposition due to an EC mechanism and the linearity of the cited plot led to a sweep rate of 1.2 V/s for the cyclic voltammetic data analysis. Ferrocene was used as an internal standard,[8,9] and did not interfere in the oxidation of the complexes.

Preparations

Substituted arylisocyanides

The substituted isocyanides were prepared from the corresponding formamides using the phosgene method reported in the literature.[10] The formamides were prepared from the corresponding aniline and formic acid in toluene by removing water by distillation after the reaction misture had refluxed for 18 hours.

$Cr(CO)_5$ isocyanide

The pentacarbonylchromium compounds were synthesized using the following method. Hexacarbonylchromium (0.27 mmoles) was placed into a Knotes airless storage tube which was vacuum-filled with argon. Dry THF (50 mL) was transferred by cannula and the tube was placed in a Rayonet Photochemical RPR-100 Reactor with the 350 nm tubes. The solution was photolyzed for 2 hours with stirring to produce $Cr(CO)_5THF$.[11] The desired substituted isocyanide ligand (0.27 mmoles) was placed in a 100 mL airless flask (Kontes) under argon by vacuum-fill. Using standard Schlenk techniques, the Cr containing solution was transferred to the flask containing the isocyanide ligand. This solution was stirred for 1 hour during which the color changed from orange to very pale yellow. The solvent was evaporated under vacuum and the product extracted into 20 mL of hexane. The unreacted $Cr(CO)_6$ was filtered off and the product was purified by column chromatography. Silica gel (100–200 mesh) was used as the adsorbent and a 10% (by volume) benzene in hexane solution was used for elution of the products. The first fractions contained the desired products and were either colorless or very pale yellow. The solvent was removed on a rotovac, and the white or off-white powders were collected.

$Cr(CO)_5(4\text{-}CNC_6H_4CF_3)$ (**I**) *Anal. Calcd.* for $C_{13}H_4CrF_3NO_5$: C,42.99; H,1.11; Cr,14.32 F,15.69, Found: C,44.17; H,1.29; Cr,13.86; F,15.72.

$Cr(CO)_5(2\text{-}CNC_6H_4CF_3)$ (**II**) *Anal. Calcd.* for $C_{13}H_4CrF_3NO_5$: C,42.99; H,1.11; Cr,14.32 F,15.69, Found: C,42.85; H,1.31; Cr,14.46; F,15.33.

$Cr(CO)_5(4\text{-}CNC_6H_4NO_2)$ (**III**) *Anal. Calcd.* for $C_{12}H_4CrN_2O_7$: C,42.37; H,1.19; Cr,15.29 N,8.34, Found: C,42.13; H,1.42; Cr,14.66; N,8.34. The 4-nitroarylisocyanide product changed color over time, so all of the products were stored in the dry box under argon. The exact nature of this color change was not investigated.

$Cr(CO)_5(4\text{-}CNC_6H_4Cl)$ (**IV**) *Anal. Calcd.* for $C_{12}H_4ClCrNO_5$: C,43.73; H,1.22; Cl,10.76 Cr,15.78. Found: C,48.77; H,1.67; Cl,9.52; Cr,14.43. This sample was always contaminated with small amounts of the $Cr(CO)_4$ $(4\text{-}CNC_6H_4Cl)_2$. The impurity could not be separated with repeated chromatographic experiments. The amount of impurity present was sufficiently small that it did not complicate the characterization of the desired product.

$Cr(CO)_5(2\text{-}CNC_6H_4Cl)$ (**V**) *Anal. Calcd.* for $C_{12}H_4ClCrNO_5$: C,43.73; H,1.22; Cl,10.76 Cr,15.78, Found: C,44.41; H,1.64; Cl,12.58; Cr,16.59. This sample was always contaminated with small amounts of $Cr(CO)_4$ $(2\text{-}CNC_6H_4Cl)_2$. The impurity could not be separated with repeated chormatographic work. The amount of impurity present was small enough that it did not complicate the characterization.

$Cr(CO)_5(2,4\text{-}CNC_6H_3Cl_2)$ (**VI**) *Anal. Calcd.* for $C_{12}H_3Cl_2CrNO_5$: C,39.59; H,0.830; Cl,20.71 Cr,14.28, Found: C,38.87; H,0.93; Cl,20.71; Cr,14.28.

$Cr(CO)_5(2,6\text{-}CNC_6H_3Cl_2)$ (**VII**) *Anal. Calcd.* for $C_{12}H_3Cl_2CrNO_5$: C,39.59; H,0.830; Cl,20.71; Cr,14.28, Found: C,40.07; H,1.04; Cl,20.02; Cr,14.52.

$Cr(CO)_5(2,4,6\text{-}CNC_6H_3Cl_3)$ (**VIII**) *Anal. Calcd.* for $C_{12}H_2Cl_3CrNO_5$: C,36.53; H,0.510; Cl,26.69 Cr,13.05, Found: C,36.53; H,0.59; Cl,26.77; Cr,12.80.

RESULTS AND DISCUSSION

The isocyanides were allowed to react with $Cr(CO)_5.THF$ on the same day that they were synthesized. Characterization of these Cr derivatives is summarized in the spectroscopic data shown in Table 1 and 2. Compounds **IV** and **V** were found to

Table 1 Infrared and ^{13}C NMR data of $Cr(CO)_5$ (arylisocyanide) complexes.

	FTIR results[a]		
Compound $Cr(CO)_5R$ R =	ν(CN) (CM^{-1})	ν(CO) (CM^{-1}) A_1,E	^{13}C NMR[b] δ in ppm axial, equatorial
$4\text{-}CNC_6H_4CF_3$ **I**	2143	2057, 1958	217.1, 215.2
$2\text{-}CNC_6H_4CF_3$ **II**	2141	2056, 1963	217.1, 215.0
$4\text{-}CNC_6H_4NO_2$ **III**	2139	2053, 1960	217.0, 215.1
$4\text{-}CNC_6H_4Cl$ **IV**	2146	2060, 1956	217.4, 215.4
$2\text{-}CNC_6H_4Cl$ **V**	2141	2056, 1958	217.2, 215.2
$2,4\text{-}CNC_6H_3Cl_2$ **VI**	2140	2052, 1960	217.0, 215.1
$2,6\text{-}CNC_6H_3Cl_2$ **VII**	2136	2053, 1961	216.9, 215.0
$2,4,6\text{-}CNC_6H_2Cl_3$ **VIII**	2132	2047, 1961	216.6, 214.8

[a] Acetonitrite solution spectra of the compounds. The reported stretches are accurate to 1 cm^{-1}
[b] Spectra were obtained in THF-d^4 and assigned in ppm relative to the solvent (*i.e.* 67.4 ppm resonance). The reported chemical shifts are accurate to 0.1 ppm.

Table 2 Cyclic voltammetry data[a]

Compound $Cr(CO)_5R$ R =	$1/2[E_{pc}+E_{pa}]$ $E_{1/2}$	$E_{pa}\text{-}E_{pc}$	i_a/i_c
I	706 mV	82 mV	1.10
II	728 mV	75 mV	1.01
III	714 mV	80 mV	1.06
IV	683 mV	70 mV	0.99
V	708 mV	82 mV	1.18
VI	731 mV	80 mV	1.02
VII	758 mV	71 mV	0.977
VIII	771 mV	75 mV	1.09
average		77(5)[b]	1.05(5)[b]

[a] Voltammetic data were collected on 3 mM solutions of sample with 0.1M $(n\text{-butyl})_4NBF_4$ in acetonitrile. Using a scan rate of 1.2 V/sec with a Pt working, Pt auxiliary, and Ag/AgCl reference electrodes. The data were collected with IR compensation and the $E_{1/2}$ listed are accurate to 10 mV. All the data are reported *vs* ferrocene/ferrocene$^+$ couple which was observed at 448 mV *vs* reference electrode with $E_{p,c}\text{-}E_{p,a}$ = 65 mV and i_c/i_a = 1.01, at the sweep rate of 1.2 V/s.
[b] Standard deviation in the last digit.

contain small amounts of the corresponding tetracarbonyldiisocyanidechromium complex.[12] The side products were formed during the reaction of $Cr(CO)_5$.THF with the isocyanides and amount to only a few percent. Attempts to separate them by column chromatography were unsuccessful. There was a noticeable trend in the reactivity between the isocyanides and $Cr(CO)_5$.THF. The ligands 2,6-dichloro- and 2,4,6-trichloroarylisocyanides reacted much more slowly than the others, based upon the visual disappearance of the orange color. For example, the orange color of

$Cr(CO)_5$.THF disappeared within 2 minutes after the addition of 4-chloroarylisocyanide, whereas with 2,6-dichloroarylisocyanide the THF adduct persists for approximately 30 minutes. The rate of color change indicated a difference in the reactivity; this difference was not studied further.

All of the isocyanides are coordinated to the metal by the carbon atom of the isocyanide group, since there are shifts of the ν(CN) between the uncoordinated and coordinated ligands.[4,12] The observed shifts ranged from 16 to 20 cm^{-1} for the eight compounds reported.

The variations in ν(CN) of coordinated arylisocyanides was reported to not vary significantly with the electron density at the metal.[13] In **I–VIII**, however, the range in ν(CN) is 14 cm^{-1}, which is as large as the range for ν(CO) (Table 1). The ν(CN) depends on the σ and π interactions of the isocyanide ligand with the metal. The σ-donating orbital of the isocyanide is antibonding relative to the C-N bond and when the isocyanide coordinates by donating this electron pair, the ν(CN) shifts to a higher energy.[4,5] The π interaction has the opposite effect on the ν(CN), because the π^* orbitals are antiboding relative to the C-N bond.[4,5] The addition of electron density to this orbital should lower the ν(CN). Theoretical studies have shown that the variation in energy of the σ-donating orbital varies only 0.015 AU (in 2-chloro-, 4-chloro-, 2-trifluoromethyl-, 4-trifluoromethyl, and 4-nitroarylisocyanide), whereas the π-accepting orbital varies 0.05 AU.[4] Therefore, it is not unreasonable to expect a range of ν(CN) since the energy of π-accepting orbitals vary to a greater extent, but both interactions with metal have compensating effects that will minimize the net change in ν(CN).

Two carbonyl bands, which are the A_1 and E stretches, are observed in all the compounds studied. The range observed for the A_1 stretching modes was 13 cm^{-1}, whereas for the E mode the range was 7 cm^{-1}. Metal carbonyl stretching frequencies are known to vary as a function of electron density at the metal.[14] The relatively small range of ν(CO) suggests that there is only a small change in then net electron exchange of compounds **I–VIII**. Likewise, the ^{13}C chemical shifts of the carbonyls are a function of the metal's electron density (Table 1).[15,16] Both resonances in **I–VIII** (*i.e.*, for the equatorial and axial carbonyls) have chemical shifts upfield from pentacarbonyl(triphenylphosphine)chromium and downfield from hexacarbonylchromium. The triphenylphosphine derivative has carbonyl resonances at 221.3 and 216.5 ppm.[15] The isocyanides studies in this work are weaker net electron donors than the phosphine derivative, since the phosphine complexes yield larger downfield shifts. The ^{13}C resonances of the isocyanide carbons were not clearly observed for all of **I–VIII**.[18]

Cyclic voltammetric studies of **I–VIII** give the following diagnostic results: **a)** a linear relationship between i_a and $\nu^{1/2}$ for the sweep range of 0.025 to 6 V/s (linearity breaks down at sweeps greater than 6 V/s, Figure 1); **b)** the peak current ratio (i_a/i_c) is 1.05 ± 0.05 at 1.2 V/s; and **c)** the complexes give peak to peak separation of 77 mV/s ± 5 at 1.2 V/s and, the peak separation is nearly invariant for sweeps from 0.025 V/s to about 4 V/s (note: the peak separation at slow sweeps shows some fluctuations due to slow decomposition of the compound and the upper sweep rate limit depends on the complex). Figure 2 contains a representative voltammogram. It is clear from the internal standard (ferrocene) that these complexes undergo one electron reversible oxidation just as reported in previous work on similar compounds.[1,2,19] The linear relationship i_a versus $\nu^{1/2}$ (Fig. 1) shows that the electrooxidation reaction, for these complexes, is diffusion con-

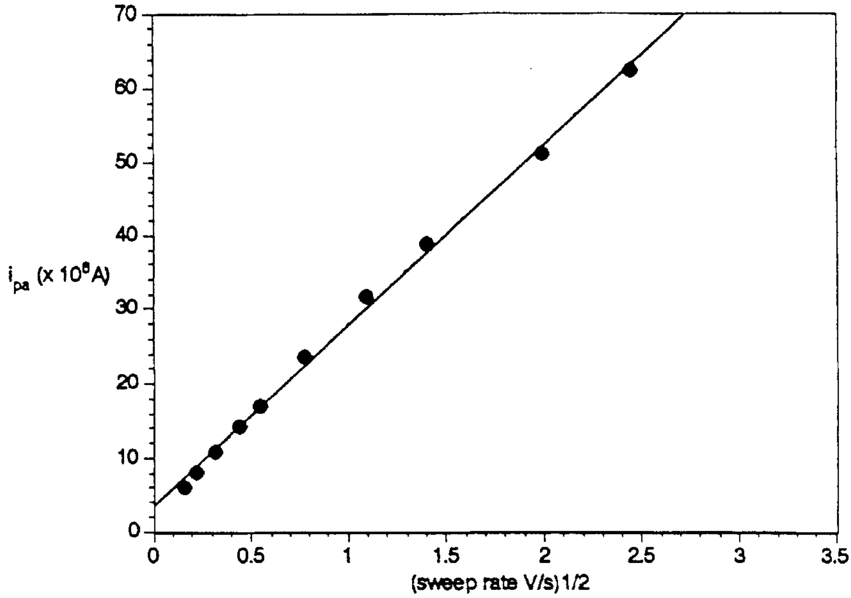

Figure 1 Relationship of i_a with $\nu^{1/2}$ for **IV**.

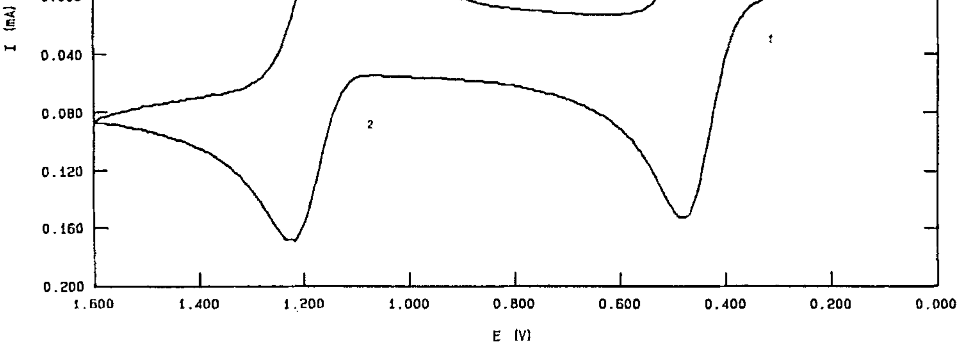

Figure 2 Cyclic voltammogram of **II** (wave 2) and the internal standard ferrocene (wave 1) is representative of all the chromium compounds studied. The voltammogram was collected on a THF solution with $TBABF_4$ (0.10M), Pt working electrode, Ag/AgCl reference electrode, and a sweep rate of 1.2 V/s.

trolled; moreover, the peak current ratios are close to 1 assuring that the selected sweep rate allows a high degree of reversibility. This permits the use of the relation $E_{1/2} = 1/2[E_{pa} + E_{pc}]$ to obtain the half potential values.[20-22] For compounds **IV** *and* **V** where the diisocyanide impurity was present, there was another small oxidation wave present in the voltammogram. The potential of the impurity was between ferrocene (the internal standard) and the wave of desired compound. The impurity did not inhibit the interpretation of data.

Potentials measured by cyclic voltammetry have been related to several parameters.[1,15,23,24] The $E_{1/2}$ of the para substituted arylisocyanide complexes (compounds **I**, **III**, and **IV**) correlate with Hammett parameters (correlation coefficient = 0.980) and less well with the σ_R (correlation coefficient = 0.962).[25] This limited set of data suggests that both the resonance and inductive contributions of the substituents are important in determining the $E_{1/2}$ of pentacarbonylisocyanidechromium compounds. Our results are consist with Treichel's work with hexaarylisocyanidechromium compounds.[2]

There also exists a relationship between the ^{13}C chemical shift and the $E_{1/2}$, since correlation coefficients of 0.943 and 0.925 for the cis and trans carbonyls, respectively, were found (Fig. 3). Similar relationships between ^{13}C carbonyl chemical shifts and force constants for carbonyl-stretching vibrations have been

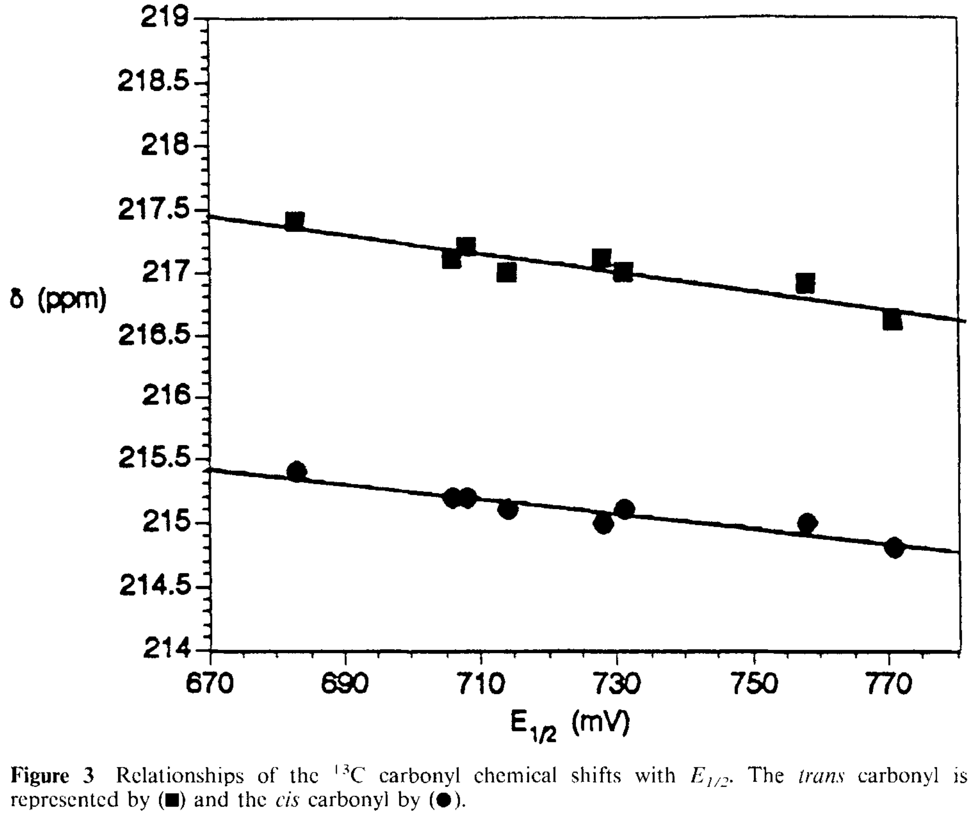

Figure 3 Relationships of the ^{13}C carbonyl chemical shifts with $E_{1/2}$. The *trans* carbonyl is represented by (■) and the *cis* carbonyl by (●).

reported and are well understood.[16] Likewise, linear relationships were found between $E_{1/2}$ and force constants for carbonyl-stretching vibrations.[23,24] Therefore the observed relationship in this study is not unreasobable even though the range of ^{13}C carbonyl chemical shifts is small. The most novel relationship is between ν(CN) and $E_{1/2}$ which yields a linear correlation coefficient of 0.925 (Fig. 4). This is the first report of a correlation (CN) of arylisocyanides with another parameter. All of the observed correlations support the importance of both the resonance and inductive effects of the substituent in determining the energy of the HOMO, since both the σ and π^* orbitals of the carbonyls and isocyanide contribute to the energy of the HOMO.[24]

Ortho substitution caused larger positive shifts $E_{1/2}$ than para substitution. For example, **II** was more difficult to oxidize than **I** by 22 mV. There are two possible explanations for this result. First, the increase in steric bulk associated with having the substituent in the ortho position prohibits the isocyanide from forming as strong a bond to chromium as the ligand with a para substituent. Alternatively the steric bulk could cause small structural changes that might effect the energy of the HOMO. Simple calculations using previously reported bond lengths[4] demonstrate that a 2-chloro group is a minimum of 4.5 Å away from the plane containing the four *cis* carbonyl ligands (assuming the metal-arylisocyanide bond length is 2.0 Å). Likewise, the fluoro atoms of the 2-trifluoromethyl substituent would be a minimum of 4.0 Å

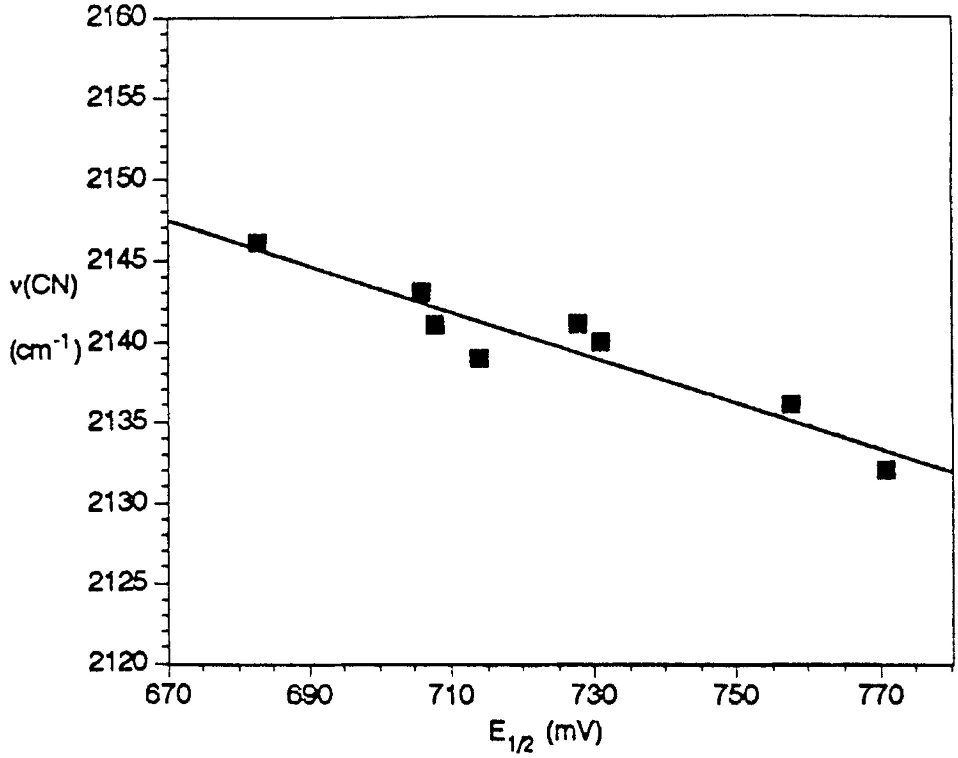

Figure 4 Relationship of ν(CN) are potential of oxidation of [Cr(CO)$_5$CNR].

away from the same plane. At these distances steric repulsion is not expected to be important. The most reasonable explanation is that the proximity of the substituent to be coordinating carbon of the isocyanide makes the isocyanide a better net electron-withdrawing ligand. Theoretical results indicate that the isocyanide ligand in **II** would be a better σ-donor and the $\pi_x{}^*$ a better acceptor than that in **I**,[4] but the theoretical results are not consistent with experimental data for **IV** and **V**.

As more substituents were added to the isocyanide ligand the $E_{1/2}$ for the chromium complexes shifted to more positive potentials. An average $\Delta E_{1/2}$ of 49 mV and 40 mV was observed upon addition of a second and third ortho-chloro substituent, respectively, to the isocyanide (Tables 2 & 3). As discussed earlier, the additional steric bulk near the coordinating carbon of the isocyanide cannot be the cause of the shifts in potential. The data demonstrate that the effect of each successively added substituent is additive with little or no decrease in the effect, since both $\Delta E_{1/2}$ are within experimental error. The $\Delta E_{1/2}$ were 23 mV and 13 mV (Table 3) when the second and third para-chloro substituent are added, respectively. Furthermore, the $E_{1/2}$ shift of the ortho substituent is twice that of the para substituent.

SUMMARY

Multiple substitution of arlyisocyanides yield ligands with a wider range of electronic and steric properties. The effects of the substituents on the electronic properties of chromium compounds are additive when several are placed on the ring. These results further support the use of substituted arylisocyanides to vary the electron density of metal centers. Clearly, more work is required to interpret how steric bulk due to ortho substitution affects the chemistry of the isocyanide and the respective metal. An important question to be addressed is whether the addition of steric bulk in the ortho positions inhibits the isocyanide insertion reactions which occurs more readily that carbonyl insertions. This problem needs to be addressed in order to use these ligands in catalytic systems.

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Table 3 Changes in $E_{1/2}$ upon addition of chloro substituents.

Location	Compounds	$\Delta E_{1/2}{}^{a}$
	Addition of second chloro substituents	
para	**VI–V**	23 mV
ortho	**VI–IV**	48 mV
ortho	**VII–V**	50 mV
	Addition of third chloro substituents	
para	**VIII–VII**	13 mV
ortho	**VIII–VI**	40 mV

[a] *a*There is a ±14 mV accuracy in these values.

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