

parameters were refined using the least-squares criteria incorporated in the digital computer simulation program EPRLQ. Listings of this program and sample input data are available on request.

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Organometallic Derivatives of the Transition Elements. I. Carbon-13 Nuclear Magnetic Resonance Studies of Bis(arene)chromium(0) Compounds

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The ^{13}C nuclear magnetic resonance spectra have been obtained for a series of bis(arene)chromium(0) compounds. The complexed arene is variously substituted by R, F, Cl, CF_3 , NR_2 , COOR. In monosubstituted bis(arene)chromium(0) complexes containing substituents which are known to perturb the resonance system of the arene, an analysis of the C-4 chemical shift indicates that in the bis(arene)chromium(0) complexes there is no transmission of substituent effects across the complexed ring. These results are interpreted to mean that a significant reduction of ring aromaticity occurs upon complexation to chromium, an effect attributed to the donation of arene π electron density into vacant metal orbitals. The reduction of ring aromaticity in the complexes explains the failure of the compounds to undergo electrophilic aromatic substitution. The availability of complexes with good leaving groups such as F and Cl, together with the reduced aromatic character of the ring, suggests nucleophilic aromatic substitution reactions on complexed rings may be feasible.

Introduction

Since Timms¹ first described the direct synthesis of bis(benzene)chromium(0) in 1969 from chromium metal atoms and benzene, a large number of bis(arene)chromium(0) complexes have been reported²⁻⁶ (as well as tungsten and molybdenum analogues) in which substituents other than alkyl or aryl groups occur. The synthesis of these new compounds has refocused attention on the structure and chemistry of the arene-metal π complexes. One of the most perplexing and, to date, unanswered structural problems associated with these compounds is the degree of aromaticity in the ligand ring upon complexation to the metal atom. The classical structural criteria for resonance delocalization in the benzene molecule are coplanarity of the six carbon atoms and equivalent C-C bond lengths. Many of the early investigations of these compounds attempted to establish D_{6h} site symmetry for the ligand in bis(benzene)chromium(0). The x-ray work of Cotton⁷ and a gas-phase electron diffraction study of bis(benzene)chromium(0) by Haaland⁸ have provided conclusive experimental evidence for sixfold symmetry of the ligand.

Several semiempirical MO descriptions of the electronic structure of bis(benzene)chromium(0) are available in the literature.⁹⁻¹⁶ In all of these treatments, the complexed ring is assumed to exhibit D_{6h} symmetry and the molecular energy levels predicted are compatible with a delocalized aromatic system but do not exclude the possibility of a reduction in aromaticity, provided that D_{6h} symmetry is maintained as the site symmetry for the ligand. Calculations place a -0.75 e charge on the ring, which is in approximate agreement with the experimentally estimated value of -0.55 e.¹⁷ Experimentally, bis(benzene)chromium(0) exhibits zero dipole moment,¹⁸ which does not necessarily imply the absence of a metal-ligand bond dipole but simply reflects the symmetrical nature of the molecule in which a net dipole cannot be detected.

The chemistry of the alkyl- and phenyl-substituted bis(arene)chromium(0) complexes prepared by the Fischer-Hafner method¹⁹ appears to be severely limited. The attainable complexes do not undergo the usual electrophilic substitution reactions characteristic of an aromatic system.²⁰ Metalation occurs with amylsodium²¹ and N,N,N',N' -tetra-

methylethylenediamine complexes of n -butyllithium.²² The complexes also exhibit base-catalyzed hydrogen-deuterium exchange.^{23,24} Nucleophilic substitution reactions have not been reported for the alkyl- and phenyl-substituted bis(arene)chromium(0) complexes which probably arise from the fact that these substituents are poor leaving groups. Semmelhack and Hall²⁵ have recently reported nucleophilic substitution reactions on chlorobenzene chromium tricarbonyl, emphasizing the electron-withdrawing character of the complexed $\text{Cr}(\text{CO})_3$ moiety.

The bis(arene)chromium(0) complexes readily undergo a one-electron oxidation to form an air-stable, water-soluble cation. It is possible that the complexed arene rings do possess a delocalized electronic system but fail to undergo the usual electrophilic substitution reactions because the electrophiles in these reactions cause oxidation of the chromium complex before the desired reaction on the ligand can go to completion. On the other hand, an effective quenching of the aromaticity of the system upon complexation may also explain the failure of the usual electrophilic substitution reactions but would be virtually impossible to detect by chemical means due to the ease of complex oxidation.

Carbon-13 magnetic resonance spectroscopy appears to be a suitable method of estimating the π -electron density in the ligand, or at least of determining the extent of perturbation occurring in the resonance system when an aromatic hydrocarbon is complexed to a metal atom. Lauterbur²⁶ suggested that variations in the local π -electron densities primarily govern the ^{13}C shieldings in aromatic rings. A good correlation was established by Spiesecke and Schneider²⁷ between the carbon chemical shift and the local π -electron density.

The quantitative estimation of the electron density at specific carbon atoms in a chemical system is a tedious process. A considerably simpler and experimentally more accessible method of estimating changes in the π -electron density is based on the chemical shift of the carbon atom para to a substituent in a monosubstituted benzene. When substituent groups such as F, OCH_3 , NR_2 , are attached to a benzene nucleus, the full effect of the π -electron perturbation, relative to benzene, is reflected in the change in chemical shift observed for C-4. This effect has been verified by both empirical and theoretical

studies.²⁸⁻³³ Beistel and Thoennis³⁴ studied the ¹H and ¹³C spectra of a series of 1,4-disubstituted benzenes and concluded that carbon-13 shifts provide a tenfold increase in sensitivity to substituent effects when compared to proton chemical shift data for the same compounds. Thus, we have at hand a strategy to investigate the state of the aromatic system in π -complexed arenes. If the transmission of resonance effects to the para carbon in the complexed ring of bis(arene)chromium(0) compounds is comparable to those observed in the free arenes, it may be concluded that no major reduction of aromaticity has occurred. Bodner and Todd³⁵ have made use of this method to estimate the perturbations in the π system with a series of monosubstituted benzenes upon complexation with Cr(CO)₃. We present here an extension of this method to bis(arene)chromium(0) compounds, in an attempt to establish clearly the extent of electronic perturbation in the arene upon complexation.

The ¹³C magnetic resonance spectra have been determined for almost all of the organic compounds used as ligands in this investigation and the spectra are thoroughly surveyed in a review by Stothers.³⁶ Several reports have appeared on the ¹³C magnetic resonance spectra of the (arene)M(CO)₃ (M = Cr, Mo, W) complexes.^{35,37-39} Our preliminary reports^{3b,40} on the ¹³C nuclear magnetic resonance results obtained in this investigation are apparently the first systematic study of bis(arene)chromium(0) complexes.

In the course of this work we have prepared 38 bis(arene)chromium(0) complexes by the cocondensation method. These complexes are variously substituted by the following functional groups: F, Cl, CF₃, R, OR, NR₂, COOR. While the results discussed in the present paper deal mainly with the mono- and polyalkyl-substituted complexes, ¹³C and ¹H NMR data have been recorded for all of the compounds prepared. The proton magnetic resonance data are discussed in a subsequent paper.

Experimental Section

Nuclear Magnetic Resonance. ¹³C NMR spectra were obtained with a Varian Associates Model HA-100 NMR spectrometer at a frequency of 25.144 MHz using a carbon probe and proton decoupling. Samples were generally analyzed as saturated benzene solutions using benzene carbon atoms as an internal standard.

¹³C spectra were obtained by two different instrumental methods.

1. For bis(arene)chromium(0) complexes of high symmetry and reasonably high solubility (50 wt %) in benzene, spectra were obtained as single scans using HR sweep with proton decoupling. A magnetic field sweep was employed in this method. Two sweeps were made, one to higher and one to lower field, to compensate for any slight field drift. The reported chemical shifts are the average of the two scans.

2. For complexes of low symmetry and low solubility in benzene, a time-average method was employed using a frequency sweep and an external deuterium lock. All spectra were proton decoupled and referenced to benzene as internal standard.

In both methods, the field width was 4 kHz.

Compounds. The metal atom reactor used in the preparation of the bis(arene)chromium(0) complexes is patterned on that reported by Timms⁴¹ and is described in detail elsewhere.⁴² All of the compounds were generally prepared using the following method described for bis(fluorobenzene)chromium(0).

Bis(fluorobenzene)chromium(0). Chromium was evaporated from metal chips (12.3 mmol) heated resistively in a close-wound, conical tungsten basket (rated at 12 V, 50 A) at a system pressure of 5×10^{-4} Torr. Fluorobenzene (0.320 mol) was cocondensed with the metal atoms on the reactor walls which were cooled to -196°C . The metal evaporation occurred over an approximately 40-min time period. After evaporation was completed, the cooling bath was removed and the reactor allowed to warm to ambient temperature under a static vacuum. The ligand-metal matrix frozen on the walls of the reactor underwent a variety of color changes as it warmed; eventually melting occurred to form a black solution. The reactor was brought to atmosphere pressure with argon and the liquid was transferred to a nitrogen-flushed flask. The excess ligand was removed on a rotary

vacuum flash evaporator, a cold finger was placed in the flask, and the product sublimed at 60°C under vacuum.⁴³ The violet crystals, 0.95 g (31.7%), were removed from the cold finger and stored in a helium-filled drybox.

Characterization of Compounds. Melting points were determined in sealed helium-filled capillaries. Low-resolution mass spectra were obtained using a Bell and Howell 21491 mass spectrometer with an ionization potential of 70 eV and a current of 7 μA . Elemental analysis of the molecular ion of the compound was performed with a Du Pont (CEC) 21-110B high-resolution mass spectrometer using a peak-matching method at a resolution of 15000 to 20000 (70 eV); perfluoroalkane was the mass standard. Chemical elemental analyses were performed (Schwarzkopf Microanalytical Laboratories) for several samples as an additional check for sample purity.

Infrared spectra were recorded as solutions in tetrachloroethylene except in a few cases in which a Nujol or Fluorolube mull was employed. A Beckman IR-7 infrared spectrometer with sodium chloride optics was used to record the spectra.

The identity and characterization of the bis(arene)chromium(0) complexes prepared in this investigation are collected in Table I. The yield reported for each compound is calculated on the basis of the initial mass of chromium metal placed in the tungsten basket and, thus, represents a minimum estimate; the true yield may be as much as 30% higher, since some of the chromium atoms condense on the internal fittings of the reactor and others recombine on the reactor walls to form finely divided chromium metal.

Halobenzene Sandwich Complexes. We have observed that bromobenzene and iodobenzene do not form complexes with chromium atoms but undergo a coupling reaction to form biphenyl and a hygroscopic green solid which is probably a chromium halide.

Contrary to earlier reports in the literature^{4b,44} we have not encountered indications of explosive compounds in attempted reactions with polyhalogenated benzenes. Cocondensations involving hexafluorobenzene, 1,2,3,4-tetrafluorobenzene, and 1,2,3,4-tetrachlorobenzene yielded only the starting materials with no evidence of unstable complexes. Pyrophoric chromium metal was observed in nearly every reaction performed, even those with alkyl benzenes; in our experience a small amount of finely divided chromium is always produced during the course of these reactions which may ignite if care is not taken during the workup of the products.

To make clear the scope and limitations of the synthetic method, we mention several reactions performed with a variety of organic ligands which do not give products possessing the general characteristics of bis(arene)chromium(0) complexes. Aniline, benzaldehyde, acetophenone, and benzonitrile all give black solutions following cocondensation with chromium atoms. A nonvolatile crystalline black-brown solid remains when the solvent is removed.

We are at present attempting to characterize this group of compounds. *N*-Trimethylborazine, pyridine, and thiophene give similar dark products which are nonvolatile; unfortunately they are also insoluble in the common organic solvents.

Results and Discussion

Isomeric Purity of Products. Sorokin and Petukhov⁴⁵ have reported that bis(ethylbenzene)chromium(0) and bis(isopropylbenzene)chromium(0) prepared by the reducing Friedel-Crafts method are not pure compounds but a mixture of π complexes resulting from transalkylation of the original hydrocarbon brought about by the action of the aluminum chloride catalyst. This effect has also been observed in the uncomplexed arenes.^{46,47} The isomeric purity of the cocondensation products had to be established before unambiguous nuclear magnetic resonance studies could be undertaken. Accordingly, a number of alkylbenzene sandwich compounds were prepared in which the ligand was highly substituted or in which the single substituent was highly branched and susceptible to rearrangement. Prior to a cocondensation reaction, the isomeric purity of the arene ligand was established by gas-liquid chromatography. The product of the reaction between the arene and chromium was thermally decomposed in a sealed tube. The colorless liquid product was analyzed by gas liquid chromatography. Table II gives the results of product analysis as obtained by Sorokin and Petukhov⁴⁵ and our results. It is apparent from the data that

alkyl rearrangement does not occur in the direct method of synthesis, an observation reported independently by Timms⁶ after our work had begun.

Coordination Shifts in Carbon-13 Spectra of Bis(arene)-chromium(0) Complexes. The ¹³C resonance of many olefin and arene ligands moves to higher fields upon coordination to a metal,⁴⁸⁻⁵⁵ although cases are reported in which a shift to lower fields is observed.^{56,57} In general, the resonance for the ring carbon atoms in π -bonded five- and six-membered aromatic systems moves to higher fields. The upfield shift for the half-sandwich complex, benzenetricarbonylchromium, is -35.2 ppm relative to benzene³⁵ (a negative sign indicates increased shielding), while for the full-sandwich compounds, the aryl carbon atoms in bis(benzene)chromium(0) are observed at -53.9 ppm relative to internal benzene. The source of the high-field coordination shift is poorly understood and currently is the subject of much discussion.^{48-55,58} In general, the source of the upfield coordination shift has been explained by metal-ligand bond anisotropy, change in hybridization of the ring carbon atoms, or electron density changes. Thoennes, Williams, and Trahanovsky³⁹ present an extensive discussion and correlation of existing theories for the upfield coordination shift. They conclude that all of the factors mentioned above contribute to some extent, but metal to arene back-bonding appears to exert the greatest influence on the coordination shift in the arene metal π complexes. An analysis of the anticipated back-bonding effects in benzenechromium tricarbonyl and bis(benzene)chromium(0) should explain the difference observed for the coordination shifts in these two molecules.

Saika and Slichter⁶⁰ first expressed the total screening constant of a nucleus in terms of three parameters

$$\sigma = \sigma_d + \sigma_p + \sigma' \quad (1)$$

where σ_d arises from diamagnetic electron currents on the observed nucleus, σ_p is the paramagnetic contribution arising from orbitals with intrinsic angular momentum centered on the atom of interest, and σ' includes all remaining terms for interatomic ring currents and electron circulation on other atoms. The paramagnetic term, σ_p , dominates in the case of shielding about a carbon nucleus (>90%).⁶¹ The important factors which affect this term are the charge polarization, variation in bond order, and the average excitation energy;⁶²⁻⁶⁵ the paramagnetic term of eq 1 predominantly determines the shielding about a carbon nucleus. Alger and co-workers⁶⁶ have treated this term in some detail and suggested that the paramagnetic term may be further subdivided for convenience into additional terms

$$\sigma_p = \sigma_p^{(1)} + \sigma_p^{(2)} \quad (2)$$

The term $\sigma_p^{(1)}$ employs only integrals composed of orbitals on the atom of interest and reflects variations in both the π and σ densities at this atom. Integrals of the $\sigma_p^{(2)}$ term involve orbitals on the atom of interest with other orbitals on directly bonded atoms. The $\sigma_p^{(2)}$ term depends upon both π and σ bond orders or overlap population densities. $\sigma_p^{(2)}$ resembles σ' but is not identical with it (eq 1), since it always involves an orbital on the carbon atom under study, while σ' is used for shielding fields arising solely on atoms removed by one or more bonds. Using a simple LCAO-MO method, these authors derived eq 3 to calculate the chemical shift of one

$$\delta_c = 100\Delta Q_\pi + 67\Delta Q_\sigma - 7\Delta P \quad (3)$$

trigonal carbon relative to another, usually benzene. In this expression σQ_π and ΔQ_σ are the differences in π - and σ -electron densities respectively, and ΔP is the difference of the sums of total π -bond orders (including overlap at the two carbon atoms compared). The third term corresponds to $\sigma_p^{(2)}$ in eq 2, while the first two are $\sigma_p^{(1)}$.

Equation 3 can be used to estimate, at least qualitatively, the carbon chemical shifts expected upon coordination to a metal.

1. Arene π orbital to metal bonding should decrease the π -electron density (Q_π) and also decrease the π -bond order (ΔP). Since these two terms are of opposite sign, the decrease in both values should to some extent oppose one another and produce only a relatively small shift.

2. If significant back-bonding, metal to arene antibonding donation, exists, an increase in Q_π would be predicted, but the π -bond order would decrease since donation into an antibonding MO does not contribute to the C-C bond. Because of the signs of the two terms involved in this case, the direction of the two changes reinforce one another and a large coordination shift should occur.

Trahanovsky³⁹ has estimated that interactions of the first type should produce a ¹³C coordination shift of less than 10 ppm while the second interaction should produce a large shift. The magnitude of the coordination shifts for benzenechromium tricarbonyl (-35.2 ppm) and bis(benzene)chromium (-53.9 ppm) clearly indicate a significant back-bonding effect.

Attributing the large upfield coordination shift to metal-arene back-bonding presupposes independent evidence to support the existence of back-bonding. Molecular orbital calculations for bis(benzene)chromium(0)⁶⁷ indicate an e_{2g} molecular orbital of suitable symmetry for back-donation of electron density from the metal to the complexed arene. A recent He(I) photoelectron study⁶⁸ of several arene- and cyclopentadienylmetal complexes indicates that the metal e_2 orbitals interact with the ligand e_2 orbitals which are antibonding and empty in the free ligand. Benzenechromium tricarbonyl would be expected to show much smaller back-bonding effects, since in this unsymmetrical molecule, two π acids (CO and benzene) are competing for the metal electron density. Infrared studies⁶⁹ indicate that carbonyl is a stronger π acid than benzene. Molecular orbital calculations⁷⁰ on benzenechromium tricarbonyl place a charge of +0.261 e on the ring and a charge of -0.296 e on a carbonyl ligand. It is clear from these data that only minimal back-bonding from the metal to the arene occurs in the half-sandwich complexes.

The ¹³C chemical shift for sp^2 carbon is proportional to the charge on the carbon atom, moving to higher field with increasing charge. The gradient is about -150 ppm per electron.⁷¹ Consequently, it is possible to account for the observed chemical shifts of π ligands by postulating the presence of a negative charge on the π ligand. The experimental upfield shift of 54 ppm for bis(benzene)chromium(0) obtained in this investigation requires a charge of 0.36 e on each ring, in reasonable agreement with other experiments which indicate a charge of approximately 0.55 e.¹⁷

The estimate of charge on the basis of chemical shift is only a rough qualitative approach, because the magnitude of the total screening constant undoubtedly reflects other factors besides back-bonding, notably metal-ligand bond anisotropy.

In a recent communication Evans and Norton⁷² argued that a simple explanation for the coordination shift in carbon atoms bound to metal atoms is not possible at present and that care should be exercised in attempting to treat total screening constants. While these observations appear to be justified for the gross coordination shifts, nevertheless, much useful information can be obtained concerning perturbations of the resonance system when substituent effects are considered relative to bis(benzene)chromium(0). The method considers the coordination shift as a constant factor and emphasizes the changes in ring carbon atom chemical shifts caused by the perturbing effects of substituents. In particular, the change in chemical shift of C-4 in a monosubstituted arene relative to the corresponding carbon atoms in bis(benzene)chromi-

Table I. Bis(arene)chromium(0) Compounds Prepared by Cocondensation of Chromium Atoms and Ligand Vapor

Compd	% yield	Mp, °C	Analysis		Physical characteristics
			HRMS ^a	Chemical analysis, (%)	
Bis(fluorobenzene)-chromium	31.70	204 dec; lit. ^c 96-98	Calcd for C ₁₂ H ₁₀ F ₂ Cr: 244.0153 Found: 244.0153	Calcd: C, 59.01; H, 4.14; F, 15.56 Found: C, 59.39; H, 4.38; F, 15.10	Black solid, air stable, volatile (45 °C, 10 ⁻³ Torr)
Bis(chlorobenzene)-chromium	23.60	135 dec; lit. ^c 89-90	Calcd for C ₁₂ H ₁₀ ³⁵ Cl ₂ Cr: 275.9565 Found: 275.9556	Calcd: C, 52.01; H, 3.64; Cl, 25.58 Found: C, 51.99; H 3.89; Cl, 25.26	Olive green solid, moderately air stable, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>m</i> -difluorobenzene)-chromium	19.32	170 dec	Calcd for C ₁₂ H ₈ F ₄ Cr: 279.9967 Found: 279.9973	<i>b</i>	Dark violet solid, air stable, volatile (50 °C, 10 ⁻³ Torr)
Bis(<i>m</i> -dichlorobenzene)-chromium	10.03	122.5-23.5	Calcd for C ₁₂ H ₈ ³⁵ Cl ₂ Cr: 244.0156 Found: 244.0153		Olive green, moderately air stable, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -difluorobenzene)-chromium	11.60	172-174 dec; lit. ^c 95 dec	Calcd for C ₁₂ H ₈ F ₄ Cr: 279.9967 Found: 279.9973		Dark violet, air stable, volatile (50 °C, 10 ⁻³ Torr)
Bis(<i>o</i> -fluorotoluene)-chromium	17.75	154-55.5	Calcd for C ₁₄ H ₁₄ CrF ₂ : 272.0469 Found: 272.0472	Calcd: C, 61.75; H, 5.19; F, 13.96 Found: C, 62.62; H, 6.27; F, 12.22	Black waxlike solid, oxidized by air to cation, volatile (60 °C, 10 ⁻³ Torr)
Bis(<i>m</i> -fluorotoluene)-chromium	7.39		<i>d</i>	<i>d</i>	Black waxlike solid, oxidized by air to cation, volatile (70 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -fluorotoluene)-chromium	45.99	90.5-1.5	Calcd for C ₁₄ H ₁₄ F ₂ Cr: 272.0469 Found: 272.0468		Black-purple solid, oxidized by air to cation, volatile (70 °C, 10 ⁻³ Torr)
Bis(<i>o</i> -chlorotoluene)-chromium	10.00	Begins to decompose at 137; no sharp dec pt.	Calcd for C ₁₄ H ₁₄ ³⁵ Cl ₂ Cr: 303.9878 Found: 303.9869		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -chlorotoluene)-chromium	19.51	134-135.5	Calcd for C ₁₄ H ₁₄ ³⁵ Cl ₂ Cr: 303.9878 Found: 303.9882		Green-brown solid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(<i>m</i> -chlorotoluene)-chromium	5.20	56-57	Calcd for C ₁₄ H ₁₄ ³⁵ Cl ₂ Cr: 303.9878 Found: 303.9871		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(methoxybenzene)-chromium	7.84	79.5-80.0	Calcd for C ₁₄ H ₁₆ O ₂ Cr: 268.0555 Found: 268.0562		Brown-black solid, oxidized by air to cation, volatile (60 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -methoxymethoxybenzene)-chromium	11.64	130-133	Calcd for C ₂₄ H ₂₀ O ₂ Cr: 392.0868 Found: 392.0872		Brown-black solid, oxidized by air to cation, volatile (130 °C, 10 ⁻³ Torr)
Bis(phenyl ether)-chromium	3.20	130-133	Calcd for C ₂₄ H ₂₀ O ₂ Cr: 392.0868 Found: 392.0872		Olive green solid, oxidized by air to cation, volatile (130 °C, 10 ⁻³ Torr)
Bis(<i>N,N</i> -dimethylaniline)-chromium	5.90	87.5-88.5	<i>e</i>		Red solid, oxidized by air to chromium oxide, volatile (80 °C, 10 ⁻³ Torr)
Bis(methyl benzoate)-chromium	4.02	111	Calcd for C ₁₆ H ₁₆ O ₄ Cr: 324.0454 Found: 324.0439		Red solid, moderately air stable, volatile (100 °C, 10 ⁻³ Torr)
Bis(benzene)-chromium	12.61	280-281; lit. ^f 284-285	Calcd for C ₁₂ H ₁₂ Cr: 208.0344 Found: 208.0337		Black solid, oxidized by air to cation, volatile (60 °C, 10 ⁻³ Torr)
Bis(toluene)-chromium	50.73	86.5-87.0	Calcd for C ₁₄ H ₁₆ Cr: 236.0657 Found: 236.0664		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>o</i> -xylene)-chromium	25.12	127-128	Calcd for C ₁₆ H ₂₀ Cr: 264.0970 Found: 264.0970		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>m</i> -xylene)-chromium	25.12	40	Calcd for C ₁₆ H ₂₀ Cr: 264.0970 Found: 264.0969		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -xylene)-chromium	29.00	115-116	Calcd for C ₁₆ H ₂₀ Cr: 264.0970 Found: 264.0970		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(1,3,5-trimethylbenzene)-chromium	12.96	114-116	Calcd for C ₁₈ H ₂₄ Cr: 292.1283 Found: 292.1273		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(1,2,3-trimethylbenzene)-chromium	4.60	138.5-140	Calcd for C ₁₈ H ₂₄ Cr: 292.1283 Found: 292.1279		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)

Table I (Continued)

Compd	% yield	Mp, °C	Analysis		
			HRMS ^a	Chemical analysis, (%)	Physical characteristics
Bis(1,2,4-trimethylbenzene)chromium	4.70	61.5-62.0	Calcd for C ₁₈ H ₂₄ Cr: 292.1283 Found: 292.1290		Black solid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(1,2,3,4-tetramethylbenzene)chromium	6.55	108-110	Calcd for C ₂₀ H ₂₈ Cr: 320.1596 Found: 320.1604		Black solid, oxidized by air to cation, volatile (95 °C, 10 ⁻³ Torr)
Bis(ethylbenzene)chromium	31.15		Calcd for C ₁₆ H ₂₀ Cr: 264.0970 Found: 264.0966		Black liquid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(1,2,4,5-tetramethylbenzene)chromium	20.67	189-190			Olive green solid, oxidized by air to cation, volatile (100 °C, 10 ⁻³ Torr)
Bis(<i>n</i> -propylbenzene)chromium	15.90		Calcd for C ₁₈ H ₂₄ Cr: 292.1283 Found: 292.1287		Black liquid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(isopropylbenzene)chromium	21.14	45.5-46; lit. ^g 46	Calcd for C ₁₈ H ₂₄ Cr: 292.1283 Found: 292.1281		Yellow-brown solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(<i>n</i> -butylbenzene)chromium	13.55		Calcd for C ₂₀ H ₂₈ Cr: 320.1596 Found: 320.1601		Black liquid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(isobutylbenzene)chromium	6.50		Calcd for C ₂₀ H ₂₈ Cr: 320.1596 Found: 320.1598		Black liquid, oxidized by air to cation, volatile (90 °C, 10 ⁻³ Torr)
Bis(<i>tert</i> -butylbenzene)chromium	27.33	76-78	Calcd for C ₂₀ H ₂₈ Cr: 320.1596 Found: 320.1589		Black solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(indan)chromium	17.07	107-109	Calcd for C ₁₈ H ₂₀ Cr: 288.0970 Found: 288.0972		Olive green solid, oxidized by air to cation, volatile (80 °C, 10 ⁻³ Torr)
Bis(cyclohexylbenzene)chromium	14.12	115-116.5	Calcd for C ₂₄ H ₃₂ Cr: 372.1909 Found: 372.1898		Dark yellow solid, slowly oxidized to cation in air, volatile (130 °C, 10 ⁻³ Torr)
Bis(benzotrifluoride)chromium	16.97	92.5-94	Molecular ion: <i>m/e</i> 344		Dark brown-black solid, stable in air for several days, volatile (56 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -fluorobenzotrifluoride)chromium	7.40	60.5-61	Molecular ion: <i>m/e</i> 380		Dark green solid, air stable for several days, volatile (56 °C, 10 ⁻³ Torr)
Bis(<i>p</i> -chlorobenzotrifluoride)chromium	12.32	80.5-82.5	Molecular ion: <i>m/e</i> 412		Rust brown solid, air stable, volatile (58 °C, 10 ⁻³ Torr)

^a High-resolution mass spectrometry. ^b No chemical analysis was performed. Purity was evident from mass spectrum. ^c Reference 2a.

^d The waxlike consistency of this compound made it impossible to obtain a high-resolution mass spectrum. A low-resolution mass spectrum was obtained by syringing a benzene solution of the solid into a capillary tube and evaporating the benzene in vacuo prior to analysis. ^e Due to the very low-intensity molecular ion peak, a high-resolution analysis could not be obtained. The low resolution spectrum of the same gives the expected molecular ion and fragmentation pattern. ^f Reference 58. ^g Reference 59.

Table II. Hydrocarbon Products from Thermal Decomposition of Bis(arene)chromium(0) Complexes^a

Compd	Recovered components	Per cent
Prepared by Reducing Friedel-Crafts Method ^b		
Bis(ethylbenzene)chromium(0)	Benzene	1
	Ethylbenzene	25
	Diethylbenzene	50
	Triethylbenzene	17
	?	7
Bis(isopropylbenzene)chromium(0)	Benzene	4
	Ethylbenzene	6
	Isopropylbenzene	28
	Diisopropylbenzene	46
	Triisopropylbenzene	16
Prepared by Cocondensation Method (These Results)		
Bis(toluene)chromium(0)	Toluene	100
Bis(1,2,3,4-tetramethylbenzene)chromium(0)	1,2,3,4-Tetramethylbenzene	100
Bis(<i>p</i> -xylene)chromium(0)	<i>p</i> -Xylene	100
Bis(isopropylbenzene)chromium(0)	Isopropylbenzene	100
Bis(<i>tert</i> -butylbenzene)chromium(0)	<i>tert</i> -Butylbenzene	100

^a Analyzed by gas-phase chromatography. ^b Reference 45.

um(0) should reflect the transmission of resonance effects across the complexed ring. The approach should be valid for a series of closely related compounds such as those considered in this investigation.

¹³C Chemical Shifts of Bis(methylbenzene)chromium(0) Complexes. Aryl Carbon Atom Chemical Shifts. The ¹³C chemical shifts of the aryl carbon atoms in a series of methyl-substituted benzenes have been reported,^{26,73} and the effect of the methyl substituent on the carbon atom shielding as well as additivity effects for the endocyclic carbon atoms has been discussed. An analogous series of bis(methylbenzene)chromium(0) complexes have been prepared in this investigation and the ¹³C nuclear magnetic resonance spectra obtained. Table III lists the chemical shifts for the endocyclic carbon atoms of these complexes (II-VIII).

In bis(toluene)chromium(0), the simplest case of methyl substitution, the methyl group deshields C-1 by +13.6 ppm, approximately 4.5 ppm more than for the same carbon atom in the free arene. Unlike free toluene in which C-4 is shielded by -3.1 ppm, C-4 in the complex is only slightly affected by the substituents, being deshielded by +0.4 ppm. C-2 and C-6 are somewhat more deshielded in the complex, +3.3 ppm, than

Table III. ^{13}C Ring Carbon Shielding for Some Bis(arene)chromium(0) Complexes

No.	Arene ^b	Shieldings, ^a ppm					
		C-1	C-2	C-3	C-4	C-5	C-6
I	Benzene	0.0	0.0	0.0	0.0	0.0	0.0
II	Toluene	[13.6]	3.3	0.4	0.4	0.4	3.3
III	<i>o</i> -Xylene	[14.0]	[14.0]	4.7	1.5	1.5	4.7
IV	<i>m</i> -Xylene	[13.3]	5.9	[13.3]	3.2	1.2	3.2
V	<i>p</i> -Xylene	[13.7]	0.4	0.4	[13.7]	0.4	0.4
VI	1,2,3-Trimethylbenzene	[13.3]	[13.0]	[13.3]	5.2	1.7	5.2
VII	1,2,4-Trimethylbenzene	[13.5]	[13.5]	7.1	[12.9]	4.2	5.2
VIII	1,3,5-Trimethylbenzene	[13.4]	5.5	[13.4]	5.5	[13.4]	5.5
IX	Ethylbenzene	[20.2]	1.3	0.3	0.3	0.3	1.3
X	<i>n</i> -Propylbenzene	[18.3]	2.4	0.3	0.3	0.3	2.4
XI	<i>n</i> -Butylbenzene	[18.9]	2.9	0.9	0.9	0.9	2.9
XII	Isobutylbenzene	[17.2]	3.2	0.3	0.3	0.3	3.2
XIII	<i>tert</i> -Butylbenzene	[28.4]	-2.7	-0.9	-0.9	-0.7	-2.7
XIV	Methyl benzoate	[2.8]	4.7	3.8	0.6	3.8	4.7
XV	<i>N,N</i> -Dimethylaniline	[42.4]	-10.1	-2.4	-0.5	-2.4	-10.1
XVI	Anisole	[56.6]	-8.5	-2.1	-0.5	-2.1	-8.5
XVII	Benzotrifluoride	[46.3]	-0.8	-3.1	-0.3	-3.1	-0.8
XVIII	Fluorobenzene	[65.7] ^c	-6.7	-2.4	-0.8	-2.4	-6.7
XIX	Chlorobenzene	[31.5]	1.6	4.7	0.4	4.7	1.6

^a Shieldings are given relative to bis(benzene)chromium(0) using the relationship $\delta(\text{C}_6\text{H}_6)_2\text{Cr} = \delta\text{C}_6\text{H}_6 + 53.9$. Positive signs are shifts to lower magnetic fields relative to bis(benzene)chromium(0). This procedure maintains the TMS sign convention. ^b Brackets indicate the position of the substituted carbon atoms. ^c This value was determined from the theoretical curve in Figure 2.

in the free arene, +0.6 ppm. The effect on the metal carbon atoms (C-3,5) is small in both cases but opposite in direction. For uncomplexed toluene the C-3,5 atoms are shielded by -0.2 ppm while in the complex the C-3,5 resonance is coincident with C-4 and deshielded by +0.4 ppm. These data indicate that the effect of the substituent methyl group is enhanced at C-1,2,6, is essentially equivalent at C-3,5, and is negligible at C-4 compared to the same effects in the uncomplexed arene.

Using the assigned chemical shifts for bis(toluene)chromium(0), the chemical shifts for the endocyclic carbon atoms in the complexes of the three isomeric xylenes can be predicted by simple additivity relationships. The predicted values are within 1 ppm of those observed with the exception of the substituted carbon atoms in the *o*-xylene complex. A similar deviation from additivity has been observed for uncomplexed *o*-xylene⁷³ which is attributed to a steric interaction between the adjacent methyl groups. The aryl carbon atom chemical shifts for the complexes with greater methyl substitution, such as bis(pseudocumene)chromium(0), can be predicted within ± 2 ppm using additivity relationships.

^{13}C Chemical Shifts of Monosubstituted Bis(alkylbenzene)chromium(0) Complexes. The chemical shifts for the endocyclic carbon atoms in a series of monosubstituted bis(alkylbenzene)chromium(0) complexes are presented in Table III (II, IX-XIII). As is observed in the free arenes,⁷³ the meta position is least affected by the alkyl substituent. However, in marked contrast to the free arenes, the para position shows little influence due to the substituent. The para carbon atom in the uncomplexed arenes is shielded by an average of 2.8 ppm in the presence of alkyl substituents.

In the alkanes, γ substitution of a methyl group for a hydrogen atom produces a shielding effect at the carbon atom of interest on the order of -2.5 ppm. Substitution of the hydrogen atoms in toluene with methyl groups is equivalent to γ substitution relative to the carbon atoms at the ortho position. Progressive methyl substitution to give the series toluene, ethyl, isopropyl, and *tert*-butylbenzene produces⁷³ a shielding effect at the ortho carbon atom in the free ligand of approximately -1.3 ppm per methyl group added. Considering the chemical shifts of the ortho carbon atoms for the same compounds when they are complexed to chromium (Table III), a similar shielding effect occurs, with a shielding increment of -2.0 ppm for each methyl group added. The ^{13}C spectrum of the isopropylbenzene complex is not available to us, however, there is the correct expected increment of -4.0

Table IV. Comparison of the C-1 Chemical Shifts for Complexed and Uncomplexed Normal-Chain Alkylbenzenes

Arene	Bis(arene)-chromium(0) complex ^a	Uncomplexed arene ^b	Δ^c
C_6H_6	0.0	0.0	0.0
$\text{C}_6\text{H}_5\text{CH}_3$	13.6	9.1	4.5
$\text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$	20.2	15.3	5.1
$\text{C}_6\text{H}_3(\text{CH}_2)_2\text{CH}_3$	18.3	13.8	4.5
$\text{C}_6\text{H}_2(\text{CH}_2)_3\text{CH}_3$	18.9	14.6	4.3

^a Chemical shifts are given in ppm relative to bis(benzene)chromium(0). ^b Chemical shifts are given in ppm relative to benzene. ^c $\delta_{\text{complex}} - \delta_{\text{arene}}$, ppm.

ppm between bis(ethylbenzene)chromium(0) and bis(*tert*-butylbenzene)chromium(0) which accounts for the addition of two methyl groups.

The chemical shifts for the carbon atoms bearing the substituents are to lower fields in both the uncomplexed and complexed arenes. Table IV presents a comparison for a series of normal-chain alkylbenzenes. It is clear that the inductive and field effects of the substituent at C-1 in the complexes are enhanced and by a roughly equal factor through the series.

Saturated Carbon Atom Chemical Shifts. The ^{13}C chemical shifts for the sp^3 -hybridized carbon atoms in a series of monosubstituted bis(arene)chromium(0) complexes are collected in Table V. The deviation of these chemical shifts for each carbon atom from those in the uncomplexed arene⁷⁴ are also indicated. In general, the two sets of chemical shifts show the same trends. The slight increase in shielding exhibited by the α -, β -, and γ -carbon atoms in the metal complexes can be attributed to the magnetic anisotropy of the metal atom. It will be noted that the magnitude of this shielding effect attenuates as the distance from the phenyl ring and the metal center increases. The cause of the anomalously large shielding effect of the carbon atom in bis(*tert*-butylbenzene)chromium(0) is not immediately clear.

The methyl carbon atom shieldings for the bis(methylbenzene)chromium(0) complexes prepared in this investigation are presented in Table VI. Woolfenden and Grant⁷³ have made a thorough study of the ^{13}C NMR spectra of the corresponding uncomplexed arenes and the data presented here for the chromium complexes are analogous in every respect to their results. The methyl chemical shifts in the chromium complexes are in general at higher magnetic field by ~ 1.0 ppm

Table V. Shielding of sp³ Carbon Atoms in Bis(alkylbenzene)chromium(0) Complexes^a

Substituent	Position of carbon relative to ring							
	α	$\Delta\delta_c^b$	β	$\Delta\delta_c$	γ	$\Delta\delta_c$	δ	$\Delta\delta_c$
Methyl	-108.5	-1.1						
Ethyl	-100.2	-0.8	-112.1	-0.2				
<i>n</i> -Propyl	-90.9	-0.7	-102.9	-0.6	-115.0	-0.3		
<i>n</i> -Butyl	-93.3	-0.6	-93.6	+1.1	-106.3	-0.8	-114.6	0.0
Isobutyl	-83.5	<i>c</i>	-97.4	<i>c</i>	-106.6	<i>c</i>		
<i>tert</i> -Butyl	-95.1	-13.9	-97.7	-0.7				

^a Chemical shifts are given in ppm relative to internal benzene. ^b $\Delta\delta_c$ values represent the difference in chemical shift for the indicated carbon atom in the complex and free ligand, i.e., $\Delta\delta_c = \delta_{\text{complex}} - \delta_{\text{arene}}$. ^c Data not reported for this arene in ref 73.

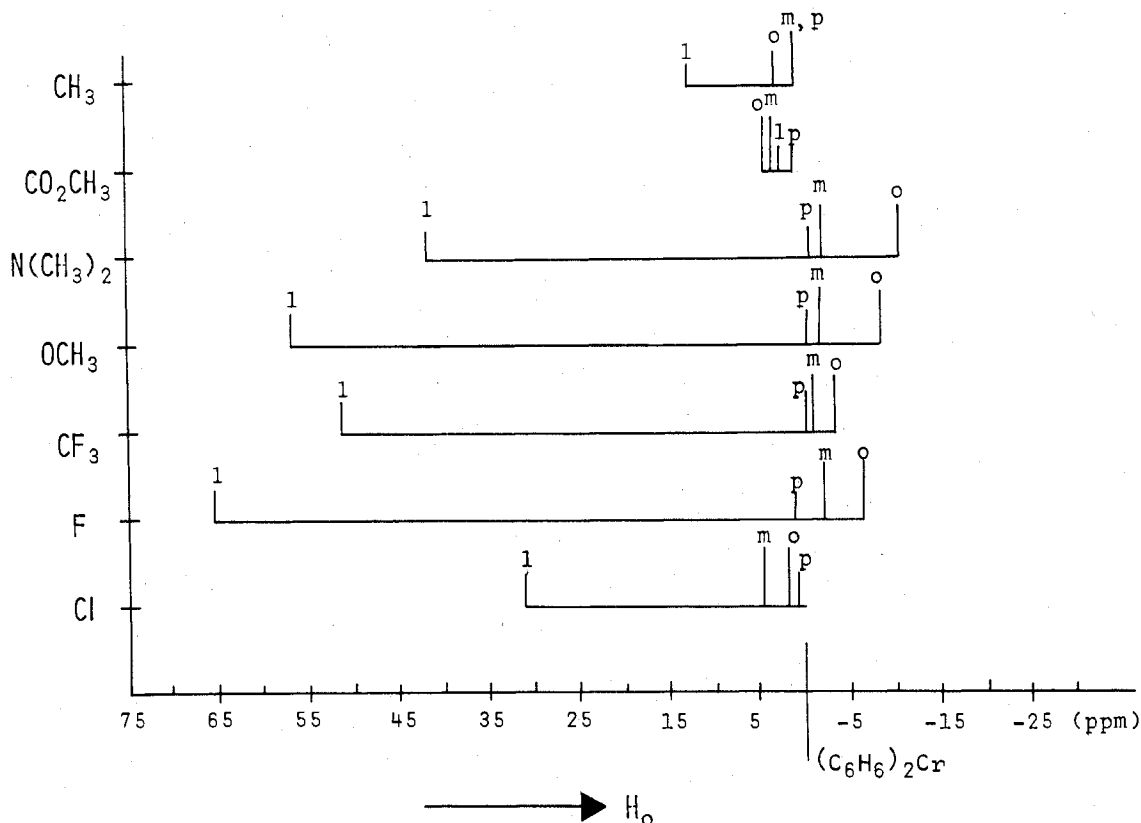


Figure 1. ¹³C chemical shifts (ppm) for the ring carbon atoms in $(C_6H_5X)_2Cr$ complexes. The number 1 represents the position of the shift of the ring carbon atom bearing the substituent (C-1); o, m, and p represent the positions of the shifts of the ortho, meta, and para carbon atoms.

than are the equivalent carbon atoms in the uncomplexed arenes. This slight increase in shielding is undoubtedly attributable to the magnetic anisotropy of the chromium atom, since a similar effect is observed for the α -carbon atom in monosubstituted alkylbenzenechromium complexes.

¹³C Chemical Shifts in Other Monosubstituted Bis(arene)chromium Complexes. The direct synthesis of organometallic complexes has made accessible a number of bis(arene)chromium(0) complexes containing substituents which are known to have a perturbing influence on σ and π systems in a free aromatic ring. A detailed study of these perturbations in the free monosubstituted benzenes has been made by Spiesbeck and Schneider²⁸ and more recently by several other workers²⁹⁻³³ using ¹H and ¹³C nuclear magnetic resonance techniques. Bodner and Todd³⁵ have used the same method to study the perturbations induced in a number of monosubstituted benzenes upon complexation with the chromium tricarbonyl moiety. This investigation extends the method and theory to the full-sandwich complexes.

The ¹³C chemical shifts for the ring carbon atoms in a series of seven monosubstituted bis(arene)chromium(0) complexes are summarized in Figure 1; numerical values are given in Table III (II, XIV-XIX).

Table VI. Methyl Carbon Atom Shieldings of the Bis(methylbenzene)chromium(0) Complexes^a

Compd	Substitution pattern of methyl groups		
	Meta or para	Ortho	Diortho
Bis(toluene)-chromium	-108.5		
Bis(<i>m</i> -xylene)-chromium	-108.4		
Bis(<i>p</i> -xylene)-chromium	-108.2		
Bis(<i>o</i> -xylene)-chromium		-110.1	
Bis(mesitylene)-chromium	-108.1		
Bis(pseudocumene)-chromium	-108.5	-110.1 [C-2] -110.1 [C-1]	
Bis(hemellitene)-chromium		-108.2 [C-1,3]	-113.3 [C-2]

^a Chemical shifts are given in ppm relative to an internal benzene standard.

C-4 Chemical Shifts. The correlation between the ¹³C chemical shift of the C-4 in monosubstituted benzenes and the

Table VII. Field and Resonance Effects Calculated Using Eq 1 for Some Related Compounds

	%	
	<i>f</i>	<i>r</i>
Uncomplexed arene	11.0	89.0
(arene)CR(CO) ₃	11.0	89.0
(arene) ₂ Cr	57.9	42.2

transmission of resonance effects has been well established.³³ Inductive and neighbor anisotropy perturbations are generally conceded to be minimal at the para position. If this view is accepted, then it is clear that the failure to observe significant shift changes at C-4 with varying substituents must be interpreted as quenching of the resonance delocalization in the ring system upon complexation. This effect was also studied in the case of arenetricarbonylchromium complexes³⁵ and an excellent linear correlation was obtained between the para carbon atom chemical shifts (both corrected and uncorrected) in the carbonyl complexes and the corresponding shifts in the free arenes; data strongly suggesting that no reduction in the ability of the π system to transmit resonance effects occurs in these complexes. Bodner and Todd³⁵ indicate that an empirical relationship exists between the chemical shift of C-4 and the field and resonance parameters proposed by Swain and Lupton⁷⁵ which is expressed in a relationship of the form

$$\int_{\text{H}}^{\text{X}} \text{C}(4) = fF_{\text{X}} + rR_{\text{X}} \quad (4)$$

where $\int_{\text{H}}^{\text{X}} \text{C}(4)$ is the change in the ¹³C NMR chemical shift of the C-4 resonance after substituting X for H at C-1; F_{X} is an inductive (including field effects) parameter and R_{X} is a resonance parameter, both characteristic for substituent X. The coefficients f and r are essentially weighting factors which indicate the relative importance of inductive and resonance effects on the change in the chemical shift at C-4 with varying substituents. These parameters are calculated by minimizing⁷⁶ the difference between the experimental chemical shifts and those calculated on the basis of eq 4. An analysis of the ¹³C NMR data obtained in the present investigation of the bis(arene)chromium(0) complexes indicates clearly that there is a significant reduction in the transmission of resonance effects across the complexed ring. No correlation exists between the C-4 chemical shifts in the free arene and the bis(arene)chromium(0) complexes. In an attempt to demonstrate, further, the reduction of resonance effects in the complexed arenes, an analysis of the ¹³C chemical shift for the C-4 resonance in the complexes was made using eq 4. The results of this analysis for the free arenes, the arenetricarbonyl derivatives, and the corresponding bis(arene)chromium(0) compounds appear in Table VII. It must be concluded from these calculations that the bonding which occurs in the bis(arene)chromium(0) complexes is essentially a π interaction between the aromatic rings and the metal, in which the arene π system is strongly perturbed. A strong π interaction of this type is predicted by molecular orbital theory¹⁴ since ligand and metal orbitals of the appropriate symmetry are available. The ¹³C data presented here represent the first direct experimental evidence which demonstrates the reduction of aromaticity in the complexed arene rings as implied by MO calculations.

The failure of the aromatic rings in the bis(arene)chromium(0) complexes to undergo electrophilic aromatic substitution can now be explained by the fact that the resonance interaction in the π system of the arene rings is essentially quenched by interaction with the vacant metal orbitals. A certain amount of this electron density may be placed back on the rings by a back-bonding mechanism through the e_{2g} orbitals;⁶⁸ this back-donation into antibonding orbitals would not be expected to contribute to stabilization of the aromatic

Table VIII. C-1 Chemical Shifts for Free Arene, Arenetricarbonylchromium, and Bis(arene)chromium(0) Complexes

Substituent	C-1 Chem shift, ppm		
	Arene ^a	(arene)-Cr(CO) ₃ ^b	(arene) ₂ Cr ^c
F	34.74	52.66	65.7 ^d
Cl	6.29	19.66	31.5
CH ₃	9.04	16.85	13.6
OCH ₃	31.50	50.18	56.6
CO ₂ CH ₃	2.88	1.50	2.8
N(CH ₃) ₂	22.22	42.18	42.4
CF ₃	-9.00 ^e		46.3

^a Relative to benzene. Data from ref 35. ^b Relative to benzenetricarbonylchromium. Data from ref 35. ^c Relative to bis(benzene)chromium(0). Data from present work. ^d Obtained from plot of C-1(complex) vs. C-1(free arene), Figure 2. ^e Reference 77.

system. On the basis of these conclusions, it might be expected that the bis(arene)chromium(0) complexes which contain good leaving groups such as F and Cl would be highly susceptible to nucleophilic aromatic substitution. Work is presently under way in this laboratory to investigate the scope of nucleophilic substitution in these complexes.

C-1 Chemical Shifts. The chemical shift of the carbon atom bearing the substituent is considered to reflect essentially the inductive and field effects of the substituent and exhibits the greatest range of values of any of the ring carbon atoms. Table VIII summarizes the C-1 chemical shifts for the uncomplexed arene, the chromium half-sandwich complexes, and the full-sandwich chromium compounds. The range of chemical shifts for both sets of complexes is considerably larger than those of the free arenes. Bodner and Todd³⁵ have concluded that the substantially larger range of C-1 chemical shifts for the complexed arenes in compounds of the type (CO)₃Cr(Ar) as compared to the uncomplexed ligands suggests an increased sensitivity to inductive substituent effects due to the net withdrawal of electron density from the σ framework of the arene ring. This argument follows from a failure to observe any perturbation in the transmission of resonance effects in the arenetricarbonylchromium complexes. Following similar arguments σ framework interactions are apparently enhanced by the reduction of π -resonance effects in the aromatic ring in our complexes.

A plot of C-1 chemical shifts of the bis(arene)chromium(0) complexes against the C-1 chemical shift of the uncomplexed arene is shown in Figure 1; the least-squares line indicated does not include bis(chlorobenzene)chromium(0). A good linear correlation ($\bar{r} = 0.99$) exists and the slope (1.90) indicates that inductive and field effects in the complexed arene are approximately twice as strong as those in the free arene. The anomalous chlorobenzene point is also observed in the data for chlorobenzene tricarbonylchromium³⁵ and indicates that C-1 in the chlorobenzene complexes is more deshielded than would be predicted by the correlation plot. The source of this decreased shielding is not immediately clear and may be due to several causes, i.e., magnetic anisotropy and steric effects. No data point for the C-1 resonance in the fluorobenzene complex is plotted, since this signal could not be detected with the instrumentation employed. Coupling of the ¹³C and ¹⁹F nuclei should give a widely spaced doublet which was undoubtedly lost in the baseline noise. Since the plot in Figure 2 is analogous in every respect to that obtained by Bodner and Todd³⁵ for the tricarbonyl complexes and these workers obtained a resonance signal for fluorobenzene which exactly fit the theoretical curve, we have used our least-squares curve and the chemical shift of C-1 in uncomplexed fluorobenzene to estimate a chemical shift of 65.7 ppm for bis(fluorobenzene)chromium(0).

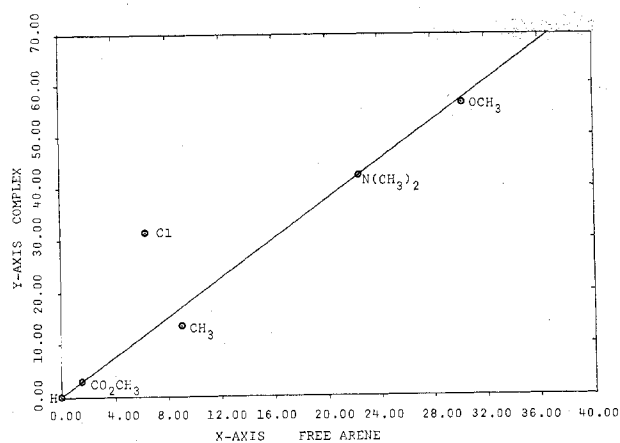


Figure 2. Plot of C-1 chemical shift (ppm) for free arene vs. the C-1 chemical shift (ppm) for the corresponding (arene)₂Cr complex.

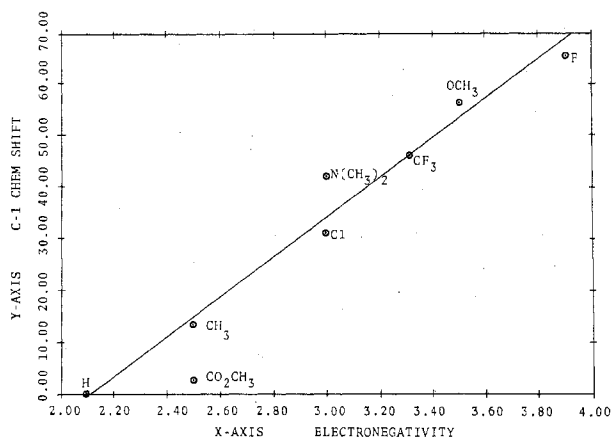


Figure 3. Plot of C-1 chemical shift (ppm) vs. electronegativity of (arene)₂Cr complexes.

Since the inductive effect of a given substituent is closely related to the electronegativity of the substituent,²⁸ a linear correlation would be expected between the C-1 chemical shift and the effective electronegativity of the substituent atom or group (Figure 3). In constructing the plot shown in Figure 3, the Pauling electronegativity of monoatomic substituents was used; for the substituent groups CH₃, OCH₃, and N(CH₃)₂, the Pauling electronegativity of the atom bonded to the ring was used; and the effective group electronegativity of 3.3 reported by Lagowski⁷⁵ was employed for CF₃. An effective group electronegativity for CO₂CH₃ is not reported in the literature so this data point is not included in the least-squares analysis. The theoretical line indicates a good correlation ($r = 0.986$) of the data which provides strong evidence that inductive effects predominate at C-1 and appear to be enhanced in the complex.

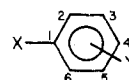
C-2,6 Chemical Shifts. The carbon atoms ortho to the substituent in the bis(arene)chromium(0) complexes are shifted in the same direction as those in the free arene, but the magnitude of the shift is only about half as large as that observed in the uncomplexed compounds. After the C-1 chemical shifts, those at C-2,6 exhibit the largest shift range.

C-3 and C-5 Chemical Shifts. The meta carbon atom chemical shifts in the complexes are only slightly affected by the substituent, exhibiting a total shift range of only 7 ppm. Although relatively small, this shift range is nevertheless larger than that observed for the free arenes which have a shift range of 2.5 ppm. A plot of the chemical shift of the meta carbon atom in the bis(arene)chromium complexes against the Hammett σ_m ⁷⁶ values for the appropriate substituent gives no apparent correlation between the two factors, an observation

Table IX. ¹³C Chemical shifts for Some Disubstituted Bis(arene)chromium(0) Complexes^a

X	Y	$\delta(\text{C}_6\text{H}_6)_2\text{Cr}$, ppm						
		1	2	3	4	5	6	CH ₃
Ortho								
CH ₃	F	6.5 ^b	<i>c</i>	-8.3 ^d	-2.1	1.1 ^e	0.1	-59.7
Meta								
CF ₃	CF ₃	<i>c</i>	0.9 ^f	<i>c</i>	1.4	-7.5	1.4	
F	F	<i>c</i>	-12.1 ^g	<i>c</i>	-5.8 ^h	-6.9 ^h	-5.8 ^h	
Cl	Cl							
CH ₃	F	11.3	-4.2 ^b	<i>c</i>	-8.5 ^b	-2.1	3.3	-56.2
CH ₃	Cl	15.1	4.9	31.6	3.9	6.8	4.3	-55.5
Para								
CF ₃	F	<i>c</i>	-2.1	-5.3	<i>c</i>	-5.3	-2.1	
CF ₃	Cl	<i>c</i>	6.9	2.2	31.3	2.2	6.9	
F	F							
CH ₃	F	14.8	0.7 ⁱ	-8.0 ^d	<i>c</i>	-8.0 ^d	-0.7 ⁱ	-55.9
CH ₃	Cl	15.4	4.4	3.9	31.5	3.9	4.4	-56.0

^a Ring carbon assignments are indicated by number



^b Doublet $J_{\text{CCF}} = 24$ Hz. ^c Not observed. ^d Doublet $J_{\text{CCF}} = 23$ Hz. ^e An extraneous unassigned peak occurs at 2.4 ppm. ^f Doublet. ^g Triplet centered at -12.1 ppm, $J = 26$ Hz. ^h Assignment tentative—based on additivity. ⁱ Doublet $J_{\text{CCCF}} = 4$ Hz. ^j Low solubility—no signals observed—400 scans.

also made for the case of the free arenes by Spiesicke and Schneider.²⁸

¹³C Chemical Shifts of Disubstituted Bis(arene)chromium(0) Complexes. A number of ortho-, meta-, and para-disubstituted bis(arene)chromium complexes were prepared during this investigation; the ¹³C NMR assignments for these compounds are summarized in Table IX. Resonance signals could not be detected for carbon atoms bearing F or CF₃ substituents with the instrumentation available. The complexes incorporating unlike meta substituents exist in two diastereomeric forms which exhibit different NMR spectra. The NMR spectrum for any such meta-substituted complex is in reality the spectra of two complexes and consequently unambiguous assignment of signals in the spectrum is impossible. The shift assignments in Table IX are only tentative and are based mainly on additivity properties. None of the series of compounds in Table IX is sufficiently complete to draw any generalizations with respect to substituent effects.

It should be pointed out that additivity effects appear to be valid even in the case of multiple substitution since most of the chemical shifts for the disubstituted complexes can be predicted to within ± 4 ppm using the values determined for the respective monosubstituted compounds.

¹³C-¹⁹F and ¹³C-¹H Coupling Constants. Although the resonance for the ring carbon atom bearing a fluorine atom could not be detected with the instrumentation available for this investigation, the resonance signals for carbon atoms two and three bonds away from the substituent were quite strong and permitted determination of the ¹³C-¹⁹F coupling constants at these positions; the two-bond value, J_{CCF} , is 24 Hz, while the three-bond value, J_{CCCF} , is 4 Hz. The carbon para to the fluorine shows a splitting of ≤ 1 Hz.

The $^1J_{\text{CH}}$ value for the complex bis(*p*-difluorobenzene)chromium(0) was determined from the carbon-13 satellite peaks in the proton spectrum; $^1J_{\text{CH}} = 174$ Hz. This value is analogous to the 174 Hz obtained for ferrocene²⁶ and the 175 Hz obtained for benzenechromium tricarbonyl.³⁵

Conclusions

¹³C studies of the bis(arene)chromium(0) complexes indicate that a drastic reduction in the transmission of resonance effects

across the complexed ring occurs. This observation is interpreted to mean that the delocalized π -electron system in a complexed arene is essentially quenched, probably as a result of donation of π -electron density into vacant metal orbitals. This reduction in aromaticity is in agreement with the observation that these complexes fail to undergo electrophilic aromatic substitution. On the basis of this interpretation and in view of the presence of good leaving groups such as F and Cl, the bis(arene)chromium(0) complexes may be expected to undergo nucleophilic aromatic substitution.

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Registry No. Bis(fluorobenzene)chromium, 42087-90-1; bis(chlorobenzene)chromium, 42087-89-8; bis(*m*-difluorobenzene)chromium, 53504-62-4; bis(*m*-dichlorobenzene)chromium, 57820-88-9; bis(*p*-difluorobenzene)chromium, 39422-94-1; bis(*o*-fluorotoluene)chromium, 53504-69-1; bis(*m*-fluorotoluene)chromium, 53504-63-5; bis(*p*-fluorotoluene)chromium, 53504-70-4; bis(*o*-chlorotoluene)chromium, 57820-89-0; bis(*p*-chlorotoluene)chromium, 57820-90-3; bis(*m*-chlorotoluene)chromium, 57820-91-4; bis(methoxybenzene)chromium, 57820-92-5; bis(*p*-methylmethoxybenzene)chromium, 57820-93-6; bis(phenyl ether)chromium, 57820-94-7; bis(*N,N*-dimethylaniline)chromium, 57820-95-8; bis(methyl benzoate)chromium, 1272-35-1; bis(benzene)chromium, 1271-54-1; bis(toluene)chromium, 12087-58-0; bis(*o*-xylene)chromium, 12092-21-6; bis(*m*-xylene)chromium, 12092-20-5; bis(*p*-xylene)chromium, 12092-22-7; bis(1,3,5-trimethylbenzene)chromium, 1274-07-3; bis(1,2,3-trimethylbenzene)chromium, 57820-96-9; bis(1,2,4-trimethylbenzene)chromium, 12243-06-0; bis(1,2,3,4-tetramethylbenzene)chromium, 57820-97-0; bis(ethylbenzene)chromium, 12212-68-9; bis(1,2,4,5-tetramethylbenzene)chromium, 57820-98-1; bis(*n*-propylbenzene)chromium, 12126-23-7; bis(isopropylbenzene)chromium, 12001-89-7; bis(*n*-butylbenzene)chromium, 12131-73-6; bis(isobutylbenzene)chromium, 51951-64-5; bis(*tert*-butylbenzene)chromium, 11081-49-5; bis(indan)chromium, 57820-99-2; bis(cyclohexylbenzene)chromium, 57821-00-8; bis(benzotrifluoride)chromium, 53966-07-7; bis(*p*-fluorobenzotrifluoride)chromium, 57821-01-9; bis(*p*-chlorobenzotrifluoride)chromium, 57821-02-0; bis(*m*-trifluoromethyl benzotrifluoride)chromium, 57821-03-1.

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