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Proton Nuclear Magnetic Resonance and Cyclic Voltammetric Studies of Mixed Bis(η^6-arene)chromium(0) Complexes from Methyl- and Trifluoromethyl-substituted Arenes

H. SSEKAALO*, J. J. LAGOWSKI and C. M. SEYMOUR

Department of Chemistry, The University of Texas, Austin, TX 78712 (U.S.A.)

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Abstract

Proton nuclear magnetic resonance and cyclic voltammetric studies were conducted on mixed bis(η^6-arene)chromium(0) compounds each containing $C_6H_{6-n}(CH_3)_n$ for half of the arene pair and $C_6H_5CF_3$ for the other half. There is more shielding of the methyl protons in $(C_6H_{6-n}(CH_3)_n)(C_6H_5CF_3)Cr$ than in $(C_6H_{6-n}(CH_3)_n)_2Cr$ contrary to expectation which should predict more shielding in the latter since CF_3 is generally regarded as an electron-withdrawing substituent. In view of this apparent anomaly, a 'two-way traffic' movement of the electron charge via the chromium atom serving as a relay for the effect of a substituent of one arene on the substituent of the other arene is proposed. It is also suggested that electron charge donation by the ligands and back-donation by chromium may be by different molecular orbital systems whereby the electron charge withdrawing power of CF_3 is more than compensated by a portion of the back-donated charge in excess of that donated by the ligands.

The preference for the formation of the complexes is in decreasing order $(C_6H_{6-n}(CH_3)_n)(C_6H_5CF_3)Cr > (C_6H_5CF_3)_2Cr > (C_6H_{6-n}(CH_3)_n)_2Cr$. The formation of $(1,2\text{-}C_6H_4(CH_3)_2)_2Cr$ was almost completely suppressed. A mechanistic model based on dipoles existing on half-sandwich species and the uncomplexed partner arene, is proposed as, perhaps, one of the possible explanations for the preferential formation of more of one complex than another.

Introduction

Several studies of mixed bis(arene) complexes of transition metals have been carried out [1–5]. Each one of these studies had objectives which dictated the choice of the arene systems used. For example, Wilburn and Skell [4] used fluorobenzene in each one of the arene pairs whose partners were set to compete for molybdenum vapour atoms. Brunner and Koch [5] used benzene as one of the members in each one of the arene pairs reacting with chromium vapour atoms. In our study, we wanted to investigate the opposing effects of electronic interactions during the formation of and in the mixed arene complexes by using an arene pair one of whose members contains electron-withdrawing and another electron-repelling substituents. Since bis(arene)chromium(0) complexes are a classic example of this type of compound, it is our view that competition reactions between the two contrasting arenes with chromium(0) could help to further the elucidation of the mechanism involved in the formation of these bis(arene)metal(0) compounds.

Preliminary work for this study was carried out using 1,2-dimethylbenzene and trifluoromethylbenzene as the competing pair for chromium vapour atoms. The products of this reaction contained practically no bis(1,2-dimethylbenzene)chromium(0). The controlled constant ligand flow rate and the fact that all of the volume of the ligands started with was pumped into the reaction flask, ensured an equal statistical chance for either ligand to be in intimate contact with the chromium atoms. Moreover, Wilburn and Skell [4] used a similar method of pumping the ligands into the reactor, but their reaction involving 1,2-dimethylbenzene and fluorobenzene, never showed such a dramatic suppression of the formation of bis(1,2-dimethylbenzene)molybdenum(0). In fact it was bis(fluorobenzene)molybdenum(0) which formed in smaller quantities than the bis(1,2-dimethylbenzene)molybdenum(0). Our work corroborates theirs with respect to the fact that each arene has an equal statistical chance of colliding with the metal atoms. In any case if either ligand did not have an equal chance of intimate collision with the chromium atoms, the mixed-arene complexes could not have formed in such larger quantities than the homo-arene complexes as has been found in the reactions studied.

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*Author to whom correspondence should be addressed. Present address: Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda.

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Against the background of this preliminary finding, we used trifluoromethylbenzene as a form of reference ligand in order to try to relate the effect of electron-withdrawing vis-à-vis electron-repelling substituents on the relative competition between arenes for chromium atoms. Besides 1,2-dimethylbenzene, the other arenes with which trifluoromethylbenzene formed a competing pair, were 1,3-dimethylbenzene, 1,4-dimethylbenzene, methylbenzene, 1,2,4-trimethylbenzene, and t-butylbenzene. As an alkyl group having a much higher electron-repelling ability than the methyl group, the t-butyl as a substituent was included in order to find out the type of change in the electron charge density environment of its protons in comparison with that of the protons of the methyl substituent.

In this study, we present ^1H NMR data, cyclic voltammetric data, and data for the relative molar amounts of the various arene chromium(0) compounds in the mixtures as aids for a systematic analysis of the factors involved in the relative preferential formation of more of one compound over another in the mixture, and in the perturbation of the electron charge density in the mixed bis(arene)-chromium(0) compounds of the type herein reported.

Experimental

Materials

Electrolytically pure chromium metal in the form of small thin plates, analytical grade arenes, benzene-d_6, and diethyl ether used as an extracting solvent for the complexes, were obtained from the Aldrich Chemical Company. The arenes and diethyl ether were dried by shaking them with molecular sieve balls first and then over sodium metal. The required quantities of arenes and diethyl ether in their feed flasks were deoxygenated by bubbling high quality nitrogen gas through them. Benzene-d_6 was dried over sodium metal.

Static Metal Vapour Atom Reactor

This metal reactor was of a basic construction similar to that used before [6, 7]. The reactor vessel port consisted of outlets to (a) a high vacuum pumping system which provided a vacuum down to a pressure of about 1×10^{-7} torr before the reaction run and about 2×10^{-6} torr during the reaction period; (b) the ligands feed flask; (c) the diethyl ether flask; (d) the excess ligands receiver flask in turn connected to another outlet leading to a separate rotary pump via a Schlenk vacuum line; and (e) a nitrogen gas supply via a Schlenk vacuum line.

Reaction Procedure

The procedure for effecting the reactions was essentially that of Graves and Lagowski [8]. However, note should be made of the following modifications. Chromium was resistively vaporized at a power rating of about 400 watts. The ligands flow rates for all reaction runs ranged between 0.30 and 0.55 $cm^3\ min^{-1}$, but the flow rate for each run was constant. In order to prevent fluctuations in the flow rate, the ligands feed flask was bathed in water warmed to between 298 and 303 K. Chromium vaporization was stopped as soon as all the ligands had been pumped into the reaction vessel. The cocondensate mixture was warmed to about 298 K at which temperature the excess ligands were pumped out and led into the excess ligands receiver flask. The complexes were extracted with successive 30 cm^3 portions of diethyl ether in order to ensure their complete removal from the cocondensate matrix. When they were freed from all the diethyl ether, they were sublimed off under vacuum and then stored under helium in a glove box from which they were obtained for any desired analysis.

Arene Exchange Reactions

Four reactions were conducted in order to establish whether or not there is any appreciable arene exchange taking place during the warm-up period. The results of this investigation are shown in Table 1. The conclusion from these results is that there is practically no appreciable arene exchange at temperatures obtained during the warm-up period. Of special interest is the reaction involving the bis(1,2-dimethylbenzene)chromium(0) in which there is practically no arene exchange even at 373 K. Thus, this shows that the arene exchange reaction is ruled out as the reason for the almost complete absence of this compound in our preliminary work.

TABLE 1. Data for testing extent of arene exchange on complexes

Complex for exchange reaction	Exchanging arene	Reaction temperature (K)	Reaction duration (min)	Result
$(1,2\text{-}C_6H_4(CH_3)_2)_2Cr$	$C_6H_5CF_3$	298	75	no exchange
$(1,4\text{-}C_6H_4(CH_3)_2)_2Cr$	$C_6H_5CF_3$	298	85	5% exchange
$(1,2\text{-}C_6H_4(CH_3)_2)_2Cr$	$C_6H_5CF_3$	348	195	no exchange
$(1,4\text{-}C_6H_4(CH_3)_2)_2Cr$	$C_6H_5CF_3$	373	80	10% exchange

Chemical Instrumentation

The mass spectra of the compounds in each one of the mixtures were recorded on Bell and Howell 21-490 and Du Pont CEC 21-110B spectrometers for low-resolution and high-resolution analysis, respectively. Both the parent and some fragmentation ions showed the characteristic chromium isotopes pattern. High-resolution mass spectrometry was used to estimate the elemental composition of each compound.

Samples for ^{1}H NMR spectroscopy were prepared in benzene-d_6 and sealed under vacuum. The spectra were recorded on a Varian Associates FT-80A spectrometer using benzene or TMS as internal reference. However, all the data for chemical shifts were reported against the TMS reference. The integrated curves under selected characteristic peaks, were each used to estimate the relative molar amount of each compound in the mixture.

Cyclic voltammetric data were obtained using linear potential peak voltammetry. These data were for the half-wave potentials of the components of each mixture as well as for their mole fractions. Diagnostic measurements on samples of each of the individual homo-arene complexes, revealed that there were no adsorption problems and that the bis(arene)$Cr^{0/+}$ redox couple was stable and reversible in a 0.20 M solution of tetra(n-butyl)ammonium hexafluorophosphate, n-Bu_4NPF_6, in tetrahydrofuran, THF. Each one of the compounds in the mixture, exhibited a one-electron oxidation in the range of −1.362 V for $(1,2\text{-}C_6H_4(CH_3)_2)_2Cr^{0/+}$ to −0.677 V for $(C_6H_5CF_3)_2Cr^{0/+}$ against the ferrocene/ferrocenium, $Cp_2Fe^{0/+}$, couple (−0.133 V). The concentration, *C*, of each component in the mixture is a function of the peak current and given by the equation

$$C = i_p/2.69 \times 10^5\, n^{3/2} A \nu^{1/2} D^{1/2} \qquad (1)$$

where i_p = peak current (A), n = number of electrons involved in the redox process, A = area of the electrode (m^2), ν = scan rate (V s^{-1}), D = diffusion coefficient (kg m^2 s^{-1}). (Values for dimensional parameters were all converted into SI units.)

The diffusion coefficient for each of the complexes was calculated by means of the Stokes-Einstein equation

$$D = kT/6\pi\eta r \qquad (2)$$

where k = Boltzmann constant, T = absolute temperature, η = viscosity coefficient, r = hydrodynamic molecular radius of the diffusing species. Here we assume that the electrolyte has a negligible effect on the viscosity and use the bulk value of 0.00461 poise for THF. The average value of r is estimated using the molar volume based on the density of the liquid bis(arene)chromium(0) compounds and obtained by means of Sterns equation

$$r = (V/8N)^{1/3} \qquad (3)$$

where V is the molar volume of the compound and N is the Avogadro number. Peak currents were measured from the decaying baseline of the preceding wave. The potential scan was stopped for approximately 20 s before initiating a scan for measuring the next peak current. Special provision was made to eliminate vibration and convection in the cell in order to ensure reproducibility. The ratio of anodic to cathodic peak currents, $i_{p,a}/i_{p,c}$, was unity in all cases.

Results

The high-resolution mass spectral data for products of the competition reactions are shown in Table 2 in which the predicted compounds for each reaction are labelled **1a**, **1b**, **1c**; 2a, **2b**, **2c**; and so on. As already pointed out in the introduction, compound **1a** for bis(1,2-dimethylbenzene)-chromium(0) was not detected by mass spectrometry because it was produced in negligible quantities. All the data indicate that the compounds in the mixture retain their molecular integrity. This served as an assurance to us that other determinations done on them while in the mixture should be as good as those done on each compound separately. A similar approach was used by Wilburn and Skell who reported equally good results of the high-resolution mass spectrometry [4].

The ^{1}H NMR data for the products of the six reactions studied are shown in Tables 3–8. The scheme used in the assignment column of these Tables for identifying the protons of the compounds in each mixture is as follows. The capital letters X, Y, and Z in brackets, designate (AA)Cr, (AB)Cr, and (BB)Cr complexes, respectively, to which the protons belong where A = $C_6H_{6-n}(CH_3)_n$, and B = $C_6H_5CF_3$. The small letters *o*, *m*, and *p* are for ring protons whose positions with reference to the substituents are *ortho*, *meta* and *para*, respectively. CH_3 identifies the methyl protons. In order to identify which ring protons are referred to in the mixed-arene complex, a subscript A or B is tagged on to Y to show which arene type these protons belong to.

The characteristic resonance peak for the methyl protons of bis(1,2-dimethylbenzene)chromium(0) is at about 2.02 ppm [9]. Therefore, its absence from Table 3 indicates that there was almost complete suppression of the formation of this compound since even at a concentration as high as 20% (wt./vol.), it was still impossible to detect this peak. The absence of this peak was put to good use since it meant that a resonance in the neighbourhood of this region should belong to the methyl protons of the mixed-arene complex.

TABLE 2. Mass spectral data for products of competition between arenes for chromium vapour atoms

Competing arene pair		Compounds predicted	HRMS[a] (*m/e*)	
A	B		Calc.	Found
1,2-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	**1a** (1,2-$C_6H_4(CH_3)_2)_2Cr$	264.0970	[b]
		1b (1,2-$C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	304.2757	304.2753
		1c $(C_6H_5CF_3)_2Cr$	344.0092	344.0096
1,3-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	**2a** (1,3-$C_6H_4(CH_3)_2)_2Cr$	264.0970	264.0965
		2b (1,3-$C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	304.2757	304.2751
		2c $(C_6H_5CF_3)_2Cr$	344.0092	344.0099
1,4-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	**3a** (1,4-$C_6H_4(CH_3)_2)_2Cr$	264.0970	264.0962
		3b (1,4-$C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	304.2757	304.2760
		3c $(C_6H_5CF_3)_2Cr$	344.0092	344.0090
$C_6H_5CH_3$	$C_6H_5CF_3$	**4a** $(C_6H_5CH_3)_2Cr$	236.0657	236.0666
		4b $(C_6H_5CH_3)(C_6H_5CF_3)Cr$	290.0375	290.0380
		4c $(C_6H_5CF_3)_2Cr$	344.0092	344.0086
1,2,4-$C_6H_3(CH_3)_3$	$C_6H_5CF_3$	**5a** (1,2,4-$C_6H_3(CH_3)_3)_2Cr$	292.3878	292.3874
		5b (1,2,4-$C_6(CH_3)_3)(C_6H_5CF_3)Cr$	318.3048	318.3052
		5c $(C_6H_5CF_3)_2Cr$	344.0092	344.0097
$C_6H_5C(CH_3)_3$	$C_6H_5CF_3$	**6a** $(C_6H_5C(CH_3)_3)_2Cr$	320.1596	320.1589
		6b $(C_6H_5C(CH_3)_3)(C_6H_5CF_3)Cr$	332.0844	332.0857
		6c $(C_6H_5CF_3)_2Cr$	344.0092	344.0089

[a] HRMS = high-resolution mass spectrometry. [b] There was practically complete suppression of the formation of (1,2-$C_6H_4(CH_3)_2)_2Cr$.

TABLE 3. ^1H NMR spectral data for compounds[a] of the 1,2-$C_6H_4(CH_3)_2$ (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[b]
1.88	singlet	6H	CH_3 (Y)
3.91	singlet	2H	*o* (Y_A)
3.98	singlet	2H	*m* (Y_A)
4.19	singlet[c]	6H	*m*, *p* (Z)
4.30	singlet	1H	*p* (Y_B)
4.35	singlet	2H	*m* (Y_B)
4.48	doublet	2H	*o* (Y_B)
4.62	d. doublets[d]	4H	*o* (Z)

[a] Predicted compound **1a** (Table 2) was not detectable by its characteristic 2.02 chemical shift for the methyl protons. [b] In this column, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para*, respectively with reference to the substituents. [c] Elsewhere [9], it was found to occur as a pseudo quartet thought possibly to be due to overlap of two triplets. [d] Occurs as a doublet of doublets.

TABLE 4. ^1H NMR spectral data for compounds of the 1,3-$C_6H_4(CH_3)_2$ (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[a]
1.88	singlet	6H	CH_3 (Y)
2.01	singlet	12H	CH_3 (X)
3.90	singlet	1H	*o* (Y_A)[b]
3.96	singlet	2H	*o* (Y_A)[c]
4.01	singlet	1H	*m* (Y_A)
4.08	singlet	8H	*o*, *m* (X)
4.17	doublet[d]	6H	*m*, *p* (Z)
4.34	singlet	3H	*m*, *p* (Y_B)
4.42	singlet	2H	*o* (Y_B)
4.59	d. doublets[e]	4H	*o* (Z)

[a] In this column, X = (AA)Cr, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para*, respectively with reference to the substituents. [b] Inside the substituents in relation to shortest distance between them around the ring. [c] Outside the substituents in relation to longest distance between them around the ring. [d] Elsewhere [9], it was found to occur as a pseudo quartet thought possibly to be due to overlap of two triplets. [e] Occurs as a doublet of doublets.

In general, there was very good agreement between the resonance peak values of this work and those in the literature [9] for the homo bis(arene)chromium(0) compounds of the six mixtures. Against this background, it was thus possible to assign the other remaining peaks to the mixed-arene complexes by difference. A collection of the data of chemical shifts of methyl protons of the mixed-arene complexes is shown in Table 9 together with that of methyl protons of the homo-arene complexes for comparison.

The oxidation potentials of the compounds for each of the mixtures are shown in Table 10. Independently prepared homo-arene complexes similar to those of the mixtures of this study, had their one-electron oxidation potentials that agreed

TABLE 5. ^{1}H NMR spectral data for compounds of the 1,4-$C_6H_4(CH_3)_2$ (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[a]
1.84	singlet	6H	CH_3 (Y)
2.01	singlet	12H	CH_3 (X)
3.97	singlet	4H	*o* (Y_A)
4.11	singlet	8H	*o* (X)
4.17	singlet[b]	6H	*m*, *p* (Z)
4.35	singlet	3H	*m*, *p* (Y_B)
4.43	d. doublets[c]	2H	*o* (Y_B)
4.63	d. doublets[c]	4H	*o* (Z)

[a] In this column, X = (AA)Cr, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para*, respectively with reference to the substituents. [b] Elsewhere [9], it was found to occur as a pseudo quartet thought possibly to be due to overlap of two triplets. [c] Occurs as a doublet of doublets.

TABLE 6. ^{1}H NMR spectral data for compounds of the C_6H_5-CH_3 (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[a]
1.83	singlet	3H	CH_3 (Y)
1.98	singlet	6H	CH_3 (X)
4.02	singlet	2H	*o* (Y_A)
4.07	doublet	3H	*m*, *p* (Y_A)
4.19[b]	singlet[c]	6H	*m*, *p* (Z)
		10H	*o*, *m*, *p* (X)
4.31	pseudo quartet	3H	*m*, *p* (Y_B)
4.52	d. doublets[d]	2H	*o* (Y_B)
4.64	d. doublets[d]	4H	*o* (Z)

[a] In this column, X = (AA)Cr, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para*, respectively with reference to the substituents. [b] The peak of these protons for the two compounds coincide; this is in agreement with the integrated area for them. [c] Elsewhere [9], it was found to occur as a pseudo quartet thought possibly to be due to overlap of two triplets. [d] Occurs as a doublet of doublets.

TABLE 7. ^{1}H NMR spectral data for compounds of the 1,2,4-$C_6H_3(CH_3)_3$ (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[a]
1.86	doublet	9H	CH_3 (Y)
1.98	singlet	18H	CH_3 (X)
3.83	singlet	3H	*o* (Y_A)
3.92	doublet	2H	*o* (Y_B)
3.96	singlet	6H	*o* (X)
4.17	triplet[b]	6H	*m*, *p* (Z)
4.34	triplet	3H	*m*, *p* (Y_B)
4.55	d. doublet[c]	4H	*o* (Z)

[a] In this column, X = (AA)Cr, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para*, respectively with reference to the substituents. [b] Elsewhere [9], it was found to occur as a pseudo quartet thought to be possibly due to overlap of two triplets. [c] Occurs as a doublet of doublets.

TABLE 8. ^{1}H NMR spectral data for compounds of the $C_6H_5C(CH_3)_3$ (A)/$C_6H_5CF_3$ (B)/Cr reaction

δ(TMS) (ppm)	Multiplicity	Area	Proton assignment[a]
1.11	singlet	9H	CH_3 (Y)
1.27	singlet	18H	CH_3 (X)
4.10	singlet	3H	*m*, *p* (Y_B)
4.17	singlet[b]	6H	*m*, *p* (Z)
4.30	singlet	6H	*m*, *p* (X)
4.33	singlet	2H	*o* (Y_A)
4.36	singlet	4H	*o* (X)
4.49	doublet	3H	*m*, *p* (Y_A)
4.57	singlet	2H	*o* (Y_B)
4.62	pseudo doublet	4H	*o* (Z)

[a] In this column, X = (AA)Cr, Y = (AB)Cr, Z = (BB)Cr; *o*, *m* and *p* are for ring protons whose positions are *ortho*, *meta* and *para* respectively with reference to the substituents. [b] Elsewhere [9], it was found to occur as a pseudo quartet thought possibly to be due to overlap of two triplets.

TABLE 9. Methyl ^{1}H NMR spectral data for products of competition between arenes for chromium vapour atoms

Competing arene pair		δ(TMS) (ppm)		Δδ[a]
A	B	(AA)Cr	(AB)Cr	
1,2-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	2.02[b]	1.88	−0.14
1,3-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	2.01	1.88	−0.13
1,4-$C_6H_4(CH_3)_2$	$C_6H_5CF_3$	2.01	1.84	−0.17
$C_6H_5CH_3$	$C_6H_5CF_3$	1.98	1.83	−0.15
1,2,4-$C_6H_3(CH_3)_3$	$C_6H_5CF_3$	1.98	1.86	−0.12
$C_6H_5C(CH_3)_3$	$C_6H_5CF_3$	1.27	1.11	−0.16

[a] Shielding value = difference between chemical shifts of mixed- and homo-arene complexes; the negative sign to the values indicates more shielding of methyl protons in mixed-arene complexes. [b] Value from Graves and Lagowski [9] since the formation of (1,2-$C_6H_4(CH_3)_2)_2$Cr was not detectable.

TABLE 10. Oxidation potentials of bis(arene)chromium(0) compounds from competition reactions of mixed arenes with chromium vapour atoms

Compound number[a]	Compound in mixture	$E_{1/2}$ (V)[b]
1a	$(1,2\text{-}C_6H_4(CH_3)_2)_2Cr$[c]	-1.344
1b	$(1,2\text{-}C_6H_4(CH_3)_2(C_6H_5CF_3)Cr$	-1.011
1c	$(C_6H_5CF_3)_2Cr$	-0.674
2a	$(1,3\text{-}C_6H_4(CH_3)_2)_2Cr$	-1.321
2b	$(1,3\text{-}C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	-1.005
2c	$(C_6H_5CF_3)_2Cr$	-0.677
3a	$(1,4\text{-}C_6H_4(CH_3)_2)_2Cr$	-1.344
3b	$(1,4\text{-}C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	-1.013
3c	$(C_6H_5CF_3)_2Cr$	-0.677
4a	$(C_6H_5CH_3)_2Cr$	-1.305
4b	$(C_6H_5CH_3)(C_6H_5CF_3)Cr$	-1.001
4c	$(C_6H_5CF_3)_2Cr$	-0.670
5a	$(1,2,4\text{-}C_6H_3(CH_3)_3)_2Cr$	-1.362
5b	$(1,2,4\text{-}C_6H_3(CH_3)_3)(C_6H_5CF_3)Cr$	-1.027
5c	$(C_6H_5CF_3)_2Cr$	-0.677
6a	$(C_6H_5C(CH_3)_3)_2Cr$	-1.242
6b	$(C_6H_5C(CH_3)_3)(C_6H_5CF_3)Cr$	-0.959
6c	$(C_6H_5CF_3)_2Cr$	-0.677

[a] Coincides with the numbering used for compound identification in Table 2. [b] In tetrahydrofuran (THF) solution of 0.2 M $n\text{-}Bu_4NPF_6$ at 298 K; potentials vs. $E_{1/2}$ of $Cp_2Fe^{0/+}$ couple (-0.133 V). [c] Cyclic voltammetry was able to detect this compound after a high amplification.

TABLE 11. Relative molar amounts of compounds from competition reactions of mixed arenes with chromium vapour atoms by ^1H NMR spectrometry

Compound number[a]	Compound in mixture	Relative molar amount (%)
1a	$(1,2\text{-}C_6H_4(CH_3)_2)_2Cr$	0.0
1b	$(1,2\text{-}C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	61.9
1c	$(C_6H_5CF_3)_2Cr$	38.1
2a	$(1,3\text{-}C_6H_4(CH_3)_2)_2Cr$	9.3
2b	$(1,3\text{-}C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	58.3
2c	$(C_6H_5CF_3)_2Cr$	32.4
3a	$(1,4\text{-}C_6H_4(CH_3)_2)_2Cr$	17.1
3b	$(1,4\text{-}C_6H_4(CH_3)_2)(C_6H_5CF_3)Cr$	58.2
3c	$(C_6H_5CF_3)_2Cr$	24.7
4a	$(C_6H_5CH_3)_2Cr$	12.0
4b	$(C_6H_5CH_3)(C_6H_5CF_3)Cr$	67.0
4c	$(C_6H_5CF_3)_2Cr$	21.0
5a	$(1,2,4\text{-}C_6H_3(CH_3)_3)_2Cr$	7.2
5b	$(1,2,4\text{-}C_6H_3(CH_3)_3)(C_6H_5CF_3)Cr$	69.1
5c	$(C_6H_5CF_3)_2Cr$	23.7
6a	$(C_6H_5C(CH_3)_3)_2Cr$	9.0
6b	$(C_6H_5C(CH_3)_3)(C_6H_5CF_3)Cr$	60.3
6c	$(C_6H_5CF_3)_2Cr$	30.7

[a] Coincides with the numbering used for compound identification in Table 2.

very well with those of the homo-arene complexes of each of the mixtures. This was another proof that the molecular integrity of the compounds of the mixtures is not affected. Although the predicted compound **1a** (Table 2) was not detectable by the other two methods, it was possible to detect it by cyclic voltammetry after a suitable amplification.

In addition to identification purposes, ^1H NMR spectroscopy was also used to determine the relative molar amounts of the compounds in each mixture without first separating them. This has an advantage of giving undoubtful quantities of the compounds actually produced since separation may lead to loss or decomposition of some amounts and then give us a false picture of the original quantities of the products. The data of the determination of the molar amounts from integrated areas below selected characteristic peaks, are shown in Table 11. It can be seen that, on the average, the formation of the mixed-arene complexes is favoured. Since NMR spectrometry is a non-destructive method and there was no ambiguity in the integrated areas, this method was used as a benchmark against which values from cyclic voltammetry could be compared. The latter method was employed on selected compounds of the mixtures on which there was also no separation done. The agreement of the results between the two methods was quite good. For example, the molar percentage of $(C_6H_5CH_3)(C_6H_5CF_3)Cr$ is 68.4 by cyclic voltammetry as compared to 67.0 by ^1H NMR spectrometry (Table 11).

Discussion

It is well established that NMR chemical shifts of various nuclei in compounds can be used as an aid to locate electronic perturbations and interactions in both σ- and π-systems of free and complexed arene ligands [3, 8–18]. Like the ring ^{13}C and substituent ^{19}F NMR resonances in bis(arene)-chromium(0) compounds [8, 16], those of the ^1H in the same compounds are also shifted upfield with reference to those in the free ligands [9]. Similar observations have also been made for bis(arene)-molybdenum(0) in respect of ^1H and ^{19}F. For the ring protons and carbons as well as the substituent fluorines, the upfield shifts were found to be comparatively large. However, the upfield shifts of resonances of protons on methyl substituents of the complexed arenes were found to be much smaller [4, 9]. In the case of the (arene)metal tricarbonyl compounds, not only were shifts of resonances of these protons small, but also often non-specific, i.e. either upfield or downfield [10].

The results of the present study show that there is a consistent upfield shift of resonances of the methyl protons of $(C_6H_{6-n}(CH_3)_n)(C_6H_5CF_3)Cr$ relative to those of $(C_6H_{6-n}(CH_3)_n)_2Cr$ (Table 9). This is surprising because we would expect a downfield shift due to the electron-withdrawing effect of the trifluoromethyl group on the partner arene. Before we attempt to account for this anomaly, we need first to examine a proposal for the origin of the upfield shifts of resonances of methyl protons in homo-arene complexes in which they occur. Some proposition would prescribe that there is a perturbation of the ring carbon electron charge in such a manner that a ring carbon does in turn conduct some of the electron charge from the metal to the methyl carbon thereby giving more shielding to its protons. The reverse movement of electron charge also goes on since we know that a methyl group is electron-repelling. Thus the ring carbon atoms act as relays between the metal and the methyl carbons. The immediate question arising out of this proposition would be to inquire whether the electron charge is conducted through the σ- or π-bond system between any two atoms possessing the two bonding orbital systems. This has been examined by several workers [13, 14, 19, 20] who proposed that the σ-bond system of the arene moiety of the complex plays a role in the electron charge movement not in any much less significant way than the π-bond system.

Van der Waals interactions of the field effects, i.e. dipole, type, have been proposed as one of the factors contributing to the increased shielding of some nuclei [21, 22]. In conjunction with this, there is experimental evidence from the work of Graves and Lagowski [8] that may be in support of this factor. They observed a much larger shielding of the tertiary carbon of the t-butyl group, $C(CH_3)_3$, in comparison with that of the methyl substituent carbons of the homo-arene chromium(0) complexes (Table 12). However, the shielding of the methyl carbons of $C(CH_3)_3$ was practically the same as that of the methyl substituent carbon. Then this would have predicted a shielding of the $C(CH_3)_3$ protons that is of the same magnitude as that of the methyl substituent protons. Therefore, the much larger shielding of the $C(CH_3)_3$ protons, may be due to the field effect interactions proposed by Caldow [21] and Buckingham *et al.* [22].

Further, there are complexes containing a methyl substituent and an electron-withdrawing substituent X. In Table 13 are shown chemical shifts of methyl protons of the simplest examples of these compounds relative to that of bis(methylbenzene)chromium(0). The methyl protons of these compounds whose arenes contain X *ortho* to the methyl group, are less shielded than those of $(C_6H_5CH_3)_2Cr$. The reverse is true for the situation where X is *meta* or *para* to the methyl group. This difference suggests that the mechanisms by which the electron charge is perturbed in the orbital systems of the two cases are different. Graves [23] pointed out that in metal-complexed arenes, substituents behave as if they are in aliphatic systems towards the ring protons especially those *ortho* to the substituents, i.e. their effect is largely σ-inductive in nature. Thus, the lesser shielding of the methyl protons *ortho* to X, may be a consequence of the inductive effect through the σ-bond relay system whereby the pull of the electron charge by the halogen through the three carbon centres is felt by these protons. Another way these protons could be less shielded is by the 'through space' dipole interactions [21, 22, 24, 25] outside the normal bond axis. Rationalization of the increased shielding of the methyl protons whose com-

TABLE 12. Chemical shifts of methyl protons of free and complexed methyl-substituted arenes

Arene	δ(TMS) (ppm)	
	$C_6H_{6-n}(CH_3)_n$	$(C_6H_{6-n}(CH_3)_n)_2Cr^a$
1,2-$C_6H_4(CH_3)_2$	2.25^b	2.02
1,3-$C_6H_4(CH_3)_2$	2.30^b	2.02
1,4-$C_6H_4(CH_3)_2$	2.30^b	2.01
$C_6H_5CH_3$	2.32^b	1.98
1,2,4-$C_6H_3(CH_3)_3$	2.25^c	1.98
$C_6H_5C(CH_3)_3$	2.30^c	1.28

[a] Data from Graves and Lagowski [9]; note excellent agreement with those of the present work (Table 9). [b] Data from collection of Varian Associates (Instrument Manufacturers). [c] Data from collection of Aldrich Chemical Company Library.

TABLE 13. Methyl ^1H NMR spectral data for methyl- and halogen-substituted arene complexes of chromium(0)

Complexed arene	δ(TMS) (ppm)^a	$\Delta\delta^b$
1,2-$C_6H_4(CH_3)F$	2.11	0.13
1,3-$C_6H_4(CH_3)F$	1.87	−0.11
1,4-$C_6H_4(CH_3)F$	1.76	−0.22
1,2-$C_6H_4(CH_3)Cl$	2.20	0.22
1,3-$C_6H_4(CH_3)Cl$	1.80	−0.18
1,4-$C_6H_4(CH_3)Cl$	1.80	−0.18

[a] Data from Graves and Lagowski [9]. [b] Shielding value relative to that of $(C_6H_5(CH_3)_2Cr$ complex; positive sign indicates deshielding, but negative value indicates more shielding.

plexes contain X *meta* or *para* to the methyl group, is even more complicated. However, one of the reasons for it may be attributed to magnetic anisotropy which is also thought to be responsible for the upfield chemical shift of the carbon of these protons [8].

Now turning our attention to the mixed-arene complexes of the present study, it is apparent that the reason for an increased shielding of the methyl protons in these compounds, cannot be any more easily explained. However, the fact that there are consistent upfield shifts of resonances of these protons that are of comparable magnitude in all these compounds studied, indicates that there is probably a common mechanism operating in all of them.

The generally held view that the trifluoromethyl group is an electron-withdrawing substituent in arene systems, seems to be disputed by some workers [24, 25]. For example, Holmes and Thomas [25] assert that it does not withdraw electron charge from the adjacent ring carbon atom, but that, rather, it repels the electron charge towards the ring. These assertions, however, do not seem to be supported by a variety of other lines of evidence that have conclusively established that the trifluoromethyl is electron-withdrawing in arene systems [26–30]. Even the half-wave potentials in Table 10, show that the CF_3 is an electron-withdrawing substituent since these potentials for the compounds in the mixture increase in the order $E_{1/2}$, (AA)Cr $<$ $E_{1/2}$, (AB)Cr $<$ $E_{1/2}$, (BB)Cr (there $A = C_6H_{6-n}(CH_3)_n$ and $B = C_6H_5CF_3$). This is in agreement with the established data to the effect that electron-repelling substituents decrease the $E_{1/2}$ value, i.e. the oxidation potential becomes more negative, while the reverse is true for electron-withdrawing substituents [27].

Unlike the compounds in Table 13, the mixed-arene chromium(0) complexes of this work, resemble the (arene)chromium(0) tricarbonyl compounds in that the interaction between the substituents of interest, must be felt through the metal atom relay. Therefore, the resultant effect of either substituent on the other, is by transmission of whatever portion of the electron charge to and fro via the appropriate molecular orbitals connecting the ligands to either side of the metal atom.

In the absence of measurements which could indicate to us the nature of the effective charge on σ- and π-orbitals at the ring carbons bonded to the methyl substituents in our mixed-arene complexes, we cannot with certainty locate which orbitals are used to conduct the electron charge from these ring carbons to the metal and vice versa. All we can say before such data are available is that the unexpected increased shielding of the methyl protons in these compounds, is a consequence of the electron charge movement and redistribution among the σ- and π-bonds such that the CF_3 plays its role of electron withdrawing which is in turn more than compensated by a portion of the back-donated charge that is in excess of the charge donated by the methyl-substituted arene. Thus, it is most likely that there exists a 'two-way traffic' movement of the electron charge via the chromium atom which serves as a relay for the effect of a substituent of one arene on the substituent of another arene.

The preferential formation of more of one compound than another in a mixture may be a consequence of the activation energy required for each one of the following steps

$$\mathrm{ACr + A \longrightarrow (AA)Cr(0)} \tag{4}$$

$$\mathrm{ACr + B \longrightarrow (AB)Cr(0)} \tag{5}$$

$$\mathrm{BCr + A \longrightarrow (AB)Cr(0)} \tag{6}$$

$$\mathrm{BCr + B \longrightarrow (BB)Cr(0)} \tag{7}$$

The assumption made here is that the formation of half-sandwich species occurs pretty fast and approximately at the same rate for either ligand. According to this prescription, the relative molar amounts of the complexes present in the mixture, is a reflection of the rates of their formation. This in turn presupposes that there is practically no ligand exchange on the products of the mixture. In fact this is supported by the data in Table 2 which show negligible arene exchange. This is in agreement with the work of Wilburn and Skell [4] and that of Johnson and Muetterties [31] in which negligible arene exchange on bis(arene)molybdenum(0) complexes was also reported.

Despite the complexity of the factors which may be dictating the magnitude of the activation energies for the steps in eqns. (4)–(7), we wish to propose a mechanistic model in the form of dipoles for the half-sandwich species and the uncomplexed partner arene. These are regarded as the source for the interaction leading to the formation of the full-sandwich species. Methylbenzene and trifluoromethylbenzene have been used as the competing arene pair for the illustration of this model (Fig. 1). As a first approximation, the methyl and trifluoromethyl groups are each shown as a whole possessing partial positive and negative poles, respectively both in the half-sandwich species and the uncomplexed arene. Therefore, among the factors which may influence the magnitude of activation energies are (i) the nature of polarity on centres (a) and (b) (Fig. 1), and (ii) the relative degree of polarity on these centres. In situations I and III, the nature of charges on centres (a) and (b) predicts attractive forces. The comparatively bigger relative molar amounts of the mixed-arene complexes obtained (Table 11), give support to the facilitating nature of the prescribed dipoles in these situations. The strength of repulsion

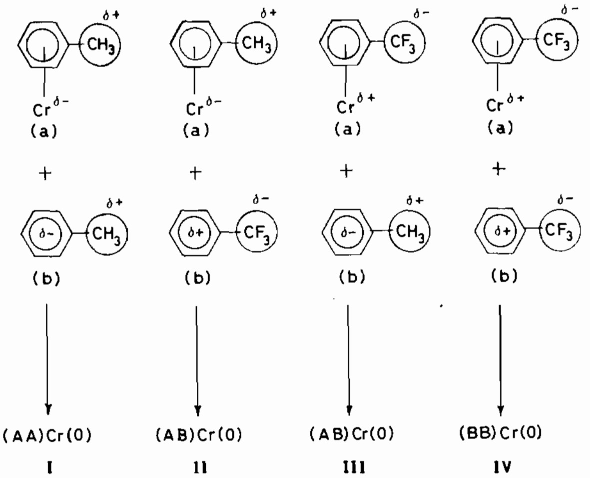

Fig. 1. Proposed mechanistic model based on the formation of dipoles as prerequisite for initiation of an activated complex leading to the full-sandwich species; the $C_6H_5CH_3/C_6H_5CF_3$ competing pair is used for illustration; (a) = Cr moiety carrying appropriate pole, (b) = uncomplexed arene ring carrying appropriate pole.

in situation I and IV for the homo-arene complex formation, should be decided by the relative charge densities on (a) and (b). A weaker repulsion will tend to make the molecular orbital overlap between the two species more facile. Indeed, this is the case in situation IV as supported by the c series of the data in Table 11. On the other hand, the formation of less quantities of the a series of homo-arene complexes should coincide with situation I.

The almost complete suppression of the formation of bis(1,2-dimethylbenzene)chromium(0) in comparison with the homo-arene complexes from the other two isomeric dimethylbenzenes, may tempt us into the conclusion that steric hindrance may be the cause of this dramatic difference. Out temptation is soon challenged by the data of the competition reaction involving 1,2,4-trimethylbenzene from which we see that a respectable quantity of bis(1,2,4-trimethylbenzene)chromium(0) was formed. Otherwise if it were steric hindrance in the case of 1,2-dimethylbenzene, then we would have expected it even to be more effective in the case of 1,2,4-trimethylbenzene. Therefore, this evidence seems to indicate that the possible existence of the proposed dipoles for initiating the activated complex, rather than steric hindrance, may be the major factor determining the rates of formation of the products of the competition reactions herein studied.

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