

# The charge distribution in substituted benzenechromiumtricarbonyl: an interpretation of spectroscopic data in terms of bond dipoles and charges

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## Abstract

The charge distribution in a series of methyl-substituted benzenechromiumtricarbonyls was investigated as a function of bond charge displacement. The modelling is based on vibrational spectroscopic data, group and bond dipole moment additivity and molecular orbital calculations. An effective radius for the chromium atom in these complexes is determined. The EXAFS spectra are related to the proposed model. © 1997 Elsevier Science S.A.

*Keywords:* Benzenechromiumtricarbonyl; EXAFS; Bond moment; Chromium charge; Infrared force constants

## 1. Introduction

The recent report [1] of an extensive infrared and Raman study of methyl-substituted benzenechromiumtricarbonyls and correlation of the spectral characteristics with molecular properties, prompted the use of a physical model [2] to probe intramolecular charge distributions. Fundamental to the bonding scheme proposed is the nature of electron displacement between the arene–chromium (Ar–Cr) and the chromiumtricarbonyl Cr(CO)<sub>3</sub> moieties with progressive methyl substitution in the coordinated arene.

To this end a diatomic bond charge model [2] for the arene–Cr(CO)<sub>3</sub>, the chromium–carbonyl (Cr–CO) and carbonyl (C–O) interactions has been adopted, where the bond charge is dependent on the vibrational force constants between the bonded groups. Using this approach it is possible to explore trends in bond charge for Ar–Cr, Cr–CO and C–O with sequential methylation of the arene ligand. The results thus obtained are correlated with EXAFS data for the complexes investigated.

For the ( $\eta^6$ -C<sub>6</sub>H<sub>6-n</sub>Me<sub>n</sub>)Cr(CO)<sub>3</sub> compounds of this study, where ( $n = 0-6$ ), the arene ligands are:  $n = 0$  benzene,  $n = 1$  toluene,  $n = 2$  *p*-xylene,  $n = 3$  mesitylene,  $n = 4$  durene,  $n = 5$  pentamethylbenzene and  $n = 6$

hexamethylbenzene. The synthesis and spectral characterisation of the complexes have been described earlier [1].

## 2. Results and discussion

### 2.1. Force constants and bond charges

The diatomic model used in Ref. [1] to obtain the arene–chromium force constants, (which we quote in Table 1 as  $k_1$ ), is also employed to determine  $k_2$  and  $k_3$ , the force constants for the Cr–CO and C–O bonds respectively. For the latter two cases the symmetric stretches of the Cr–CO and C–O bonds are used. Parr and coworkers [2,8] have applied a bond charge model for the vibrational potential energy of heteronuclear diatomic and triatomic bonded systems to determine the bond charge  $q$  which is a measure of the accumulation of charge in the bond region (bond order). The following expression was used:

$$q = \sqrt{\frac{4R^3k}{7e^2}} \quad (1)$$

where  $q$ ,  $k$ ,  $R$  (the equilibrium bond distance) and  $e$  (the electronic charge) are all in atomic units. The various force constants and bond charges so determined

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Table 1  
Equilibrium bond distances  $R$ , bond charges  $q^a$  and vibrational force constants  $k$  for  $(\eta^6\text{-C}_6\text{H}_{6-n}\text{Me}_n)\text{Cr}(\text{CO})_3$  complexes <sup>b</sup>

Molecule	$R_1/10^{-10}\text{ m}$	$k_1^c/\text{N m}^{-1}$	$q_1$	$R_2/10^{-10}\text{ m}$	$\nu(\text{sym})^d/\text{cm}^{-1}$	$k_2^c/\text{N m}^{-1}$	$q_2$	$R_3/10^{-10}\text{ m}$	$\nu(\text{sym})^e/\text{cm}^{-1}$	$k_3^c/\text{N m}^{-1}$	$q_3$
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	1.726 <sup>f</sup>	267	1.84	1.841	475	242	1.93	1.158	1975	4182	4.01
$(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$	1.725 <sup>g</sup>	305	1.97	1.823	477	244	1.91	1.151	1970	4161	3.96
$(\eta^6\text{-C}_6\text{H}_4\text{Me}_2)\text{Cr}(\text{CO})_3$	1.72 <sup>h</sup>	342	2.09	1.84	479	246	1.94	1.15	1966	4144	3.97
$(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3$	1.729 <sup>h</sup>	404	2.28	1.836	480	247	1.95	1.153	1962	4127	3.96
$(\eta^6\text{-C}_6\text{H}_2\text{Me}_4)\text{Cr}(\text{CO})_3$	1.725 <sup>i</sup>	426	2.33	1.833	479	246	1.94	1.154	1957	4106	3.95
$(\eta^6\text{-C}_6\text{HMe}_5)\text{Cr}(\text{CO})_3$	1.726 <sup>j</sup>	477	2.47	1.834 <sup>k</sup>	477	244	1.93	1.154 <sup>k</sup>	1953	4090	3.95
$(\eta^6\text{-C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$	1.726 <sup>k</sup>	519	2.57	1.836	481	248	1.95	1.155	1949	4073	3.94

<sup>a</sup> An effective electronic charge of  $-qe$  is ascribed to the bond (Parr and coworkers [2]).

<sup>b</sup> For the quantities  $R$ ,  $q$  and  $k$  the subscripts 1, 2 or 3 refer in turn to the Ar–Cr, Cr–CO or the C–O bond.

<sup>c</sup> The values of  $k_1$  are quoted from Ref. [1];  $k_2$  and  $k_3$  are calculated using data in Ref. [1].

<sup>d</sup>  $\nu(\text{sym})$  from Ref. [1], refers to the symmetric Cr–CO bond stretching vibration.

<sup>e</sup>  $\nu(\text{sym})$  from Ref. [1], refers to the symmetric C–O bond stretching vibration.

<sup>f</sup> Ref. [3].

<sup>g</sup> Ref. [4].

<sup>h</sup> Ref. [5].

<sup>i</sup> Ref. [6].

<sup>j</sup> The values of  $R$  for  $(\eta^6\text{-C}_6\text{HMe}_5)\text{Cr}(\text{CO})_3$  are assumed. Due to the uniformity of the  $R$  distances within the series, an error of less than 0.5% is expected.

<sup>k</sup> Ref. [7].

are presented in Table 1, with the bond charges also graphed in Fig. 1.

Examining the bond charge values, a striking feature is the near constancy of those for the Cr–CO and C–O bonds, as opposed to the substantial increase of the  $q$  values in the arene–chromium bond with progressive arene methylation. This suggests that the major electron reorganization occurring with methyl substitution is located in the arene–Cr segment of the molecule. Further, the analysis indicates that the arene–Cr bond charge  $q_1$  and the bond order is increasing with methylation. This result accords with infrared and Raman evidence in Ref. [1], with <sup>95</sup>Mo NMR spectral results for the analogous molybdenum complexes [9], and with trends in spectroscopic and thermodynamic data found in methylated ferrocenes [10,11].

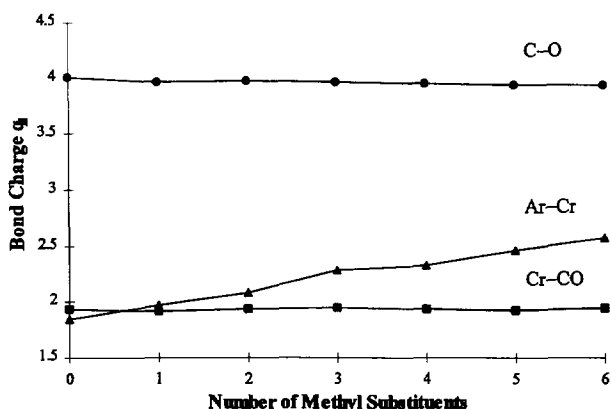


Fig. 1. Variation of bond charge with methylation for the Ar–Cr ( $q_1$  ▲), Cr–CO ( $q_2$  ■) and C–O ( $q_3$  ●) bonds.

## 2.2. The bond charge parameter of displacement $\alpha$ and effective one-dimensional box length $\gamma R$

Parr and coworkers [2] have related the bond dipole  $\mu$  to the displacement of the bond charge  $q$  away from the mid-point of a bond. Applying this approach to the arene–chromium system, we locate the charge  $q$  at a distance  $R_{\text{Cr}}$  from the chromium atom, so that  $R_{\text{Cr}} = (R_1/2)(1 + \alpha)$ , where  $R_1$  is the arene–chromium bond length and  $\alpha$  an increment of this length. The expression for  $\mu$  follows (in atomic units) as

$$\mu = e \frac{R_1}{2} [Z_{\text{Cr}} - Z_{\text{Ar}} + q_1 \alpha] \quad (2)$$

$$= e \frac{R_1}{2} [2Z_{\text{Cr}} + q_1(\alpha - 1)] \quad (3)$$

As indicated in Table 1, the subscript 1 refers to the arene–chromium bond. On the basis of the Parr model [2],  $Z_{\text{Cr}} + Z_{\text{Ar}} = q_1$  and this simplifies the initial expression for  $\mu$  to that in Eq. (3).  $Z_{\text{Cr}}$  and  $Z_{\text{Ar}}$  are the charges appropriate to the chromium atom and the arene ring respectively. Values of  $R_1$  and  $q_1$  for the series of complexes studied are given in Table 1. It remains to obtain assessments of  $\mu$  and  $Z_{\text{Cr}}$ .

The vibrational analysis in Ref. [1] has indicated that the integrated infrared intensities of the arene–chromium bond decrease with progressive methylation. This intensity is a measure [12] of the change in dipole moment  $\mu$  with change in vibrational state along a normal coordinate  $Q$ , i.e.  $\partial\mu/\partial Q$  measured at the equilibrium position. If it is assumed that the coordinate is associated with purely a bond stretch, and further that

Table 2

Bond dipole moments  $\mu(\text{Ar}-\text{Cr})$ , charge displacements  $\alpha$  and effective free-electron one-dimensional box lengths  $\gamma_i R_i$  for  $(\eta^6\text{-C}_6\text{H}_{6-n}\text{Me}_n)\text{Cr}(\text{CO})_3$  complexes

Molecule	Relative infrared intensity <sup>a</sup>	$\mu(\text{Ar}-\text{Cr})$ <sup>b</sup> /Debye	$\alpha$	$\gamma_1 R_1/10^{-10}$ m	$\gamma_2 R_2/10^{-10}$ m	$\gamma_3 R_3/10^{-10}$ m
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	1.000	5.47	0.60	1.67	1.69	0.93
$(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$	0.992	5.42	0.59	1.62	1.69	0.93
$(\eta^6\text{-C}_6\text{H}_4\text{Me}_2)\text{Cr}(\text{CO})_3$	0.780	4.26	0.52	1.57	1.68	0.93
$(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3$	0.405	2.22	0.40	1.51	1.68	0.93
$(\eta^6\text{-C}_6\text{H}_2\text{Me}_4)\text{Cr}(\text{CO})_3$	0.237	1.30	0.36	1.49	1.68	0.93
$(\eta^6\text{-C}_6\text{HMe}_5)\text{Cr}(\text{CO})_3$	0.166	0.91	0.34	1.45	1.68	0.93
$(\eta^6\text{-C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$	0.115	0.63	0.34	1.42	1.68	0.94

<sup>a</sup> Infrared intensities taken from Ref. [1] and normalised to that of benzenechromiumtricarbonyl.<sup>b</sup> The value of  $\mu(\text{Ar}-\text{Cr})$  herein is derived from the product of the relative infrared intensity and  $\mu(\text{Bz}-\text{Cr}) = 5.47\text{D}$ .

the charge separation across the bond is unaffected by the vibrational state, then the infrared intensity can be taken to relate approximately to the ground state bond moment—see Armstrong et al. [1]. If the bond dipole  $\mu(\text{Bz}-\text{Cr})$  in  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  were known, then an Ar–Cr bond moment for a methylated analogue could be estimated by multiplying  $\mu(\text{Bz}-\text{Cr})$  by the ratio of the infrared intensities.

From trends observed for the Ar–Cr infrared intensities, it has been deduced that the dipole vector of the benzene–Cr bond in  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  is directed from Cr (positive) to the benzene (negative) and that the metal–arene dipole moment diminishes with methyl substitution on the arene [1]. This result is in qualitative accord with atomic charge distributions from XPS [13], CNDO/2 [14,15] and SCCC [16–18] studies. Armstrong et al. [1] particularly cite Kinomura et al. [13] who found that in benzenechromiumtricarbonyl the benzene possesses a charge of  $-0.12e$ , chromium  $+0.54e$ , (carbonyl) carbon  $+0.15e$  and oxygen a charge of  $-0.29e$ . These charges lead to a benzene–Cr bond dipole moment  $\mu(\text{Bz}-\text{Cr})$  of 5.47 D and an  $\alpha$  of  $0.60 \times 10^{-10}$  m. On the basis of this  $\mu(\text{Bz}-\text{Cr})$  and the ratio of the infrared intensities relative in each case to that of

benzenechromiumtricarbonyl, we calculate  $\mu(\text{Ar}-\text{Cr})$  and  $\alpha$  values for the  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  series. These are listed in columns 3 and 4 of Table 2.

The variation of  $\alpha$  with the number of substituents is shown in Table 2. This, together with parallel estimates of  $\alpha$  using different charge distributions from other MO calculations, is also displayed in Fig. 2. In all cases examined,  $\alpha$  decreases with increasing methylation, providing clear evidence for progressive displacement of electron charge density away from the coordinated arene and towards the chromium. If the charge distributions of Kinomura et al. [13] are used, the effective bond charge  $q_1$  for the Bz–Cr bond is located relatively close ( $0.35 \times 10^{-10}$  m) to the benzene ring. With methyl group insertion,  $q_1$  progressively relocates further from the arene reaching a limiting distance of  $0.57 \times 10^{-10}$  m for the  $\text{C}_6\text{Me}_6$  complex. The results with the charge distributions from Refs. [14,19] are closely similar. Those based on the charges of Hillier and coworkers [16,17] lead to  $\alpha$  values which are not physically meaningful for the earlier members of the series ( $n = 0-3$ )<sup>1</sup> but approach the  $\alpha$  values of the earlier calculations for the more highly methylated complexes.

If one envisages in this model that the limiting value of  $\alpha$  gives the point of closest approach of  $q_1$  to the chromium (beyond which it would experience a net repulsion by the chromium atom electron density) then this could be taken to define the effective chromium radius. On this basis the latter is estimated as  $(R_1/2)(1 + \alpha_{\text{lim}})$ . Using  $\alpha_{\text{lim}} = 0.34$  (from Table 2) we calculate an effective chromium radius as  $1.16 \times 10^{-10}$  m. A comparison is made with the radius expected (approximately) for a chromium atom of charge  $+0.54$ , obtained assuming linearity between the radii of Cr(0), Cr(2+) and Cr(3+) from Ref. [20], which is found to be ca.  $1.13 \times 10^{-10}$  m. The two estimates are in surprisingly good agreement.

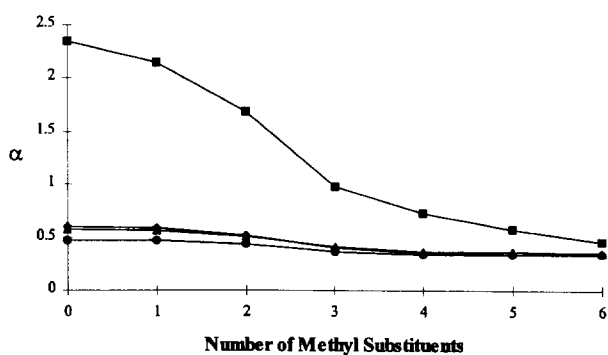


Fig. 2. Variation of  $\alpha$  with methylation and choice of charge distribution: ◆,  $\alpha$  as a function of  $Z_{\text{Cr}} = +0.54$ , Ref. [13]; ▲,  $\alpha$  as a function of  $Z_{\text{Cr}} = +0.486$ , Ref. [14]; ■,  $\alpha$  as a function of  $Z_{\text{Cr}} = +2.08$ , Refs. [16,17]; ●,  $\alpha$  as a function of  $Z_{\text{Cr}} = +0.504$ , Ref. [19]. Note that the two sets of points ◆ and ▲ are superimposed in the graph, as are those of ● for the latter values of  $n$ .

<sup>1</sup> For example, according to these charge distributions  $q_1$  for benzene chromium tricarbonyl is located  $2.88 \times 10^{-10}$  m from Cr, i.e.  $1.15 \times 10^{-10}$  m beyond the benzene of the  $\text{C}_6\text{H}_6\text{-Cr}$  bond.

Another parameter which can be used to gauge the mobility of the bond charge  $q$  derives from a model which supposes that the  $q$  electrons move free-electron-like in a one-dimensional box of length  $\gamma R$ . Eq. (4), quoted from Ref. [2] (p. 59), is used to obtain  $\gamma$  (in units of bond length  $R$ ):

$$\gamma^4 = \left( \frac{h^4}{28m^2e^2} \right) \left( \frac{1}{kR^5} \right) \quad (4)$$

where  $h$  is Planck's constant and  $m$  is the electronic mass (all are in atomic units). The results are included in columns 5–7 of Table 2 and a graph of  $\gamma_i R_i$  against the degree of methylation in Fig. 3. As for  $q_2$  and  $q_3$ , the  $\gamma_2 R_2$  and  $\gamma_3 R_3$  values for the Cr–CO and C–O bonds are seen to be almost invariant in the series. By contrast,  $\gamma_1 R_1$  is seen to decrease substantially with methyl substitution in the arene indicating a progressive reduction in the free path length for electrons in the Ar–Cr bond.

### 2.3. Bond charge displacement and the Cr 1s threshold energy

Direct evidence can be obtained for electron density variations at the chromium atom from the Cr 1s electron threshold energies as determined by EXAFS analysis [5]. Of particular interest is the position of the leading K-edge of the X-ray absorption spectrum. Attempts have been made to correlate such data with several factors [21], including the effective nuclear charge of the metal, electronegativity differences between pairs of bonded atoms of the metal–ligand groupings, and the ionic radius of the central metal atom. Of these factors, the ligand electronegativity in the arenechromiumtricarbonyls would be expected to experience little change due to the constancy of the bonded atoms in the series. A second-order perturbation to the arene ligand electronegativity may arise with increasing electron donor character upon methylation; for the carbonyl ligands,

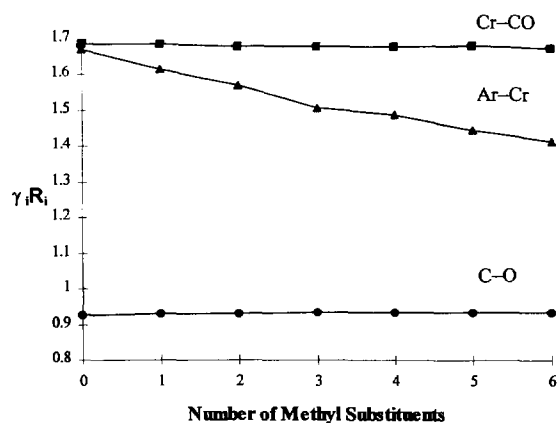


Fig. 3. Variation of  $\gamma_i R_i$  with methylation (units of  $10^{-10}$  m) for the Ar–Cr ( $\gamma_1$ ,  $\blacktriangle$ ), Cr–CO ( $\gamma_2$ ,  $\blacksquare$ ) and C–O ( $\gamma_3$ ,  $\bullet$ ) bonds.

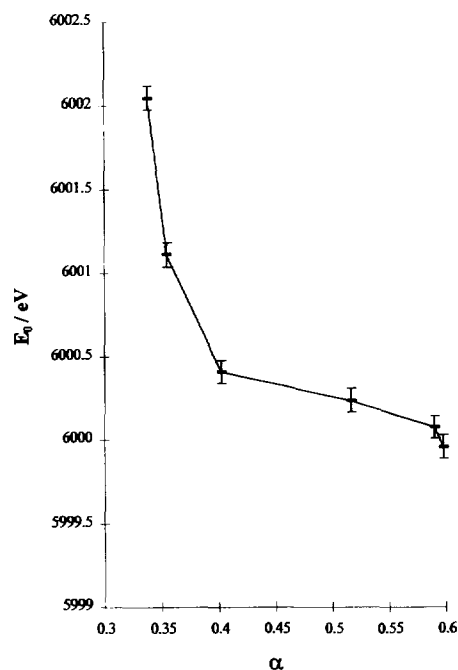


Fig. 4. Variation of the Cr 1s threshold energies with the arene–chromium bond parameter  $\alpha$  for the  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  complexes;  $\alpha$  relates to  $Z_{\text{Cr}} = +0.54$  from Ref. [13]. The  $E_0$  values, which were derived using the statistical procedure of Ref. [23], have an error of  $\pm 0.07$  eV.

this would be even less significant as indicated from the bond charges in Table 1. The near constancy of bond distances for all ligands in the series suggests also that charge variations on the chromium atom may be small. An analogous situation was found to apply to a series of methyl-substituted ferrocenes [22] where it was shown that, even for decasubstitution, there is no substantial change in the charge on the iron atom.

A plot of the calculated threshold energy  $E_0$  against  $\alpha$ , the location of the arene–chromium bond charge, in Fig. 4, shows that these parameters are related, albeit in a non-linear fashion, indicating a dependence of  $E_0$  on  $\alpha$  and hence  $R_{\text{Cr}}$ . As  $\alpha$  decreases with methylation of the arene, the bond charge  $q_1$  is displaced closer to the chromium. A concomitant increase occurs in the  $q_1$  values as seen in column 4 of Table 1. Such results correlate well with conclusions from the spectroscopic studies of Refs. [1,5,24].

### 3. Conclusions

Application of the physical treatment of Parr and coworkers [2,8] to methyl-substituted benzenechromiumtricarbonyl complexes has shown that: (i) the Ar–Cr bond charge in  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  is located relatively close to the benzene ligand; (ii) with sequential methylation, the arene–chromium bond charge and bond order increase and progressive bond charge displace-

ment occurs away from the arene towards Cr and that a limiting distance from the chromium is reached; (iii) a reduction occurs in the free path length of electrons within the Ar–Cr bond with increasing methylation; (iv) the increasing Cr 1s threshold energy (with progressive methylation) correlates with the increasing Ar–Cr bond charge and decreasing  $R_{Cr}$  distance.

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