Molecular Electrostatic Potential and Electron Density Topography: Structure and Reactivity of (substituted arene)Cr(CO)$_3$ Complexes

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Structural properties as well as subtle electronic effects occurring in (substituted arene)-Cr(CO)$_3$ complexes have been investigated at HF, B3LYP, and MP2 levels using the topographical properties of the molecular electrostatic potential (MESP) as well as electron density. The most stable structures are characterized as syn-eclipsed for an electron-donating arene substituent and anti-eclipsed for an electron-withdrawing arene substituent. The MESP topography unambiguously revealed the electronic nature of the Cr(CO)$_3$ moiety as a very strong electron-withdrawing group to the arene unit of the complex. Interestingly, the substituent effects are strongly felt at the MESP surrounding the carbonyl oxygen rather than the arene ring. The effect of electron correlation significantly changes the values of the MESP at CPs, especially in the case of systems with an electron-withdrawing substituent. The electron density topography revealed that only the three ring carbon atoms that are syn with respect to the carbonyl groups are bonded to the chromium atom via a (3, −1) bond critical point, suggesting a trigonal-prismatic structure for these complexes.

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Introduction

The structure and reactivity of a substituted arene are altered significantly on complexation with a transition-metal moiety.[1,2] For instance, it is mainly susceptible to nucleophilic substitutions rather than electrophilic substitutions.[1,2] This difference is attributed to the strong electron-accepting power of the metallic moiety that is coordinated to the arene ring in an η^6 fashion.[3] Another property is its ability to undergo highly diastereoselective and enantioselective addition reactions.[2] Further, these stereochemically enriched species show interesting geometrical modifications at the arene ring depending on the nature of the arene substituent. For instance, from a systematic X-ray crystallographic study of (η^6-arene)Cr(CO)$_3$ complexes, Hunter et al.[4] have discovered that the π-donor substituents and their ipso carbons are bent away from the Cr(CO)$_3$ group, whereas π-acceptor substituents and their ipso carbons lean slightly toward the Cr(CO)$_3$ group. Another geometric feature is that the conformation of the metallic moiety with respect to the substituted arene ring is strongly dependent on the nature of the arene substituent.[5] In general, the Cr(CO)$_3$ moiety prefers a syn-eclipsed conformation for an electron-donating group and an anti-eclipsed conformation for an electron-withdrawing group[5] (cf. Figure 1). It is also noticed that the electron flow toward Cr(CO)$_3$ proceeds more effectively when the arene ligand has a donor substituent. In comparison to the free arene systems, sometimes complexed arene systems show striking differences from the normal orientation effect (ortho−para-directing or meta-directing effect toward an electrophilic attack) of the substituent.[2] However, we notice that though the orientation effect of a substituent on a free aromatic ring is well-established, it is not very clear in the case of a complexed aromatic system. This is mainly due to the unstable nature of the arene complexes toward electrophiles as well as due to the deactivation of the arene ring toward commonly used electrophiles, restricting any systematic experimental studies. However, theoretical studies employing modern computational techniques are expected to offer convenient ways of exploring various structure- and reactivity-related features of the arene complexes. In this paper, we mainly explore the subtle electronic effects that occur in various chromium substituted arene

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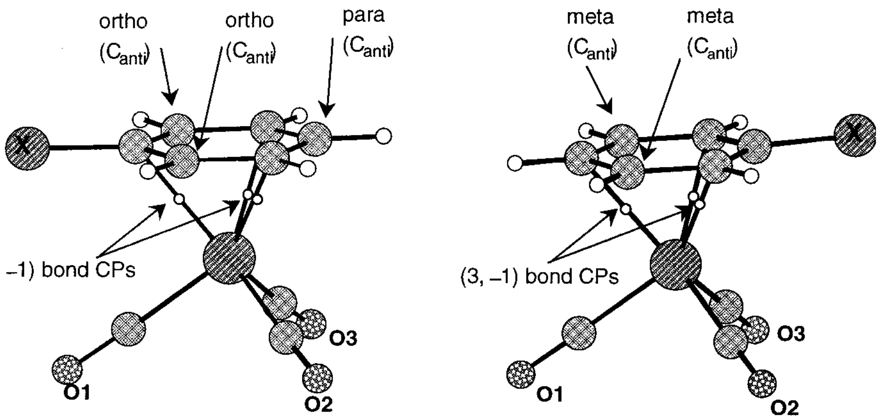

Figure 1. (a, left) Syn-eclipsed and (b, right) anti-eclipsed conformations of (substituted (X) arene)chromium carbonyl complexes. MESP minima are generally observed near the C_{anti} carbon atoms.

carbonyl complexes by rigorous topography mapping of molecular scalar fields.

The topographical studies of scalar fields[6−8] are very useful in understanding the various features of the physicochemical behavior of a molecule. For example, the topological details such as local minima and first-order saddle points of the potential energy surface of a molecular system are very much used for interpreting reaction mechanisms as well as chemical dynamics. Recent works can be found in the literature which interpret the topological details of the molecular scalar fields such as electron density and electrostatic potential into chemically useful information for understanding the structure, bonding, and interactive behavior of molecular systems. In fact, these two experimentally observable quantities stand as the most important scalar fields of a molecule for understanding a wide variety of chemical phenomena.[9−12]

It has been recently found that the scalar field of molecular electrostatic potential (MESP) topography can give a very clear indication of the orientation effects of a substituent on an aromatic ring.[13] In singly substituted benzenoid systems, negative MESP minima are observed near the ortho and para carbons for ortho−para-directing groups and near the meta carbons for meta-directing groups. In addition, in these systems, the MESP values at the critical points (CP) located near the meta and para carbon atoms showed linear correlations with the Hammett σ_m and σ_p constants,[14] respectively. Even features such as π-bonds, bent bonds, lone pair regions, etc. could be revealed by the MESP topography.[15] The positions as well as values of the MESP at CPs give a fairly good idea about the regioselectivities of a molecular system toward an electrophile or a nucleophile.

Bader et al.[16] have pioneered topographical studies on molecular electron density, $\rho(\mathbf{r})$, and successfully employed it for an exhaustive study of the molecular structure. Their investigations have revealed that a bond in a molecule is generally represented by a (3, −1) saddle known as a bond CP, a ring in a molecular frame shows up as a (3, +1) saddle, and a cage gives rise to a (3, +3) minimum in $\rho(\mathbf{r})$ distribution. Other parameters such as bond ellipticity[17,18a] and bond orders, which are expressed respectively in terms of eigenvalues and electron density values at the bond CP, are also quite useful in the study of phenomena such as charge delocalization and have been applied for a wide variety of aromatic systems. The topography mapping of electron density is even employed in determining the structure and bonding of van der Waals complexes.[18b,c] The present work primarily uses the MESP as well as $\rho(\mathbf{r})$ topographical features to understand the subtle

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electronic effect of a substituent in chromium substituted arene carbonyl complexes.

Theoretical Methods

The aim of the present work is to study the structure- and reactivity-related features of a chromium substituted arene carbonyl complex in terms of the MESP as well as electron density topography. Some representative arene substituents (NH_2, OH, CH_3, F, CHO, CN, NO_2) are chosen so as to cover the main electronic effects such as induction, resonance, and hyperconjugation. All the complexes in their syn-eclipsed as well as anti-eclipsed conformations (cf. Figure 1) have been studied (including geometry optimizations as well as MESP and electron density topography calculations) using the Gaussian94[19] set of programs at ab initio HF/6-311G and B3LYP/6-311G levels[20,21] of theory. Some selected complexes have been also studied using a general basis set (Gen) at HF, B3LYP, and MP2 levels wherein the 6-31G* basis set is used for all the heavy elements other than chromium; for chromium and hydrogen the 6-311G and 6-31G basis sets are used, respectively.

The scalar field of molecular electrostatic potential (MESP), $V(\mathbf{r})$, at a point $\mathbf{r}$ due to a molecular system with nuclear charges $\{Z_A\}$ located at $\{\mathbf{R}_A\}$ and the electron density $\rho(\mathbf{r})$ is defined as

$$V(\mathbf{r}) = \sum_{A}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \tag{1}$$

where N is the total number of nuclei in the molecule. This quantity can also be regarded as the energy required for bringing a proton from infinity to a point $\mathbf{r}$ at the unperturbed ground state of the molecule. In other words, the $V(\mathbf{r})$ values have the physical meaning of the energetic behavior of a molecule interacting with a test positive charge.[22−27] The most characteristic feature of $V(\mathbf{r})$ is that it takes negative as well as positive values, depending on which term in eq 1 is dominating at the point $\mathbf{r}$. For example, near the nuclear framework of the molecule, $V(\mathbf{r})$ is always positive due to the extreme dominance of the nuclear term over the electronic term. On the other hand, lone pair and π-bond regions normally show high negative values for MESP, reflecting the highly concentrated distribution of electrons in those regions. Note that any change in the environment surrounding the lone pair or the π-regions due to the attachment of a new substituent to the system or its complexation would lead to a corresponding change in the $V(\mathbf{r})$ values at those regions. Evaluation of the topological properties of $V(\mathbf{r})$, e.g., the maxima, minima, and saddle points on the MESP surface, provides a very convenient tool for monitoring the subtle electronic changes that occur during such situations. The maxima, minima, and saddle points are called critical points (CPs) of MESP. They are characterized by the number of eigenvalues of their Hessian matrix (second-derivative matrix of $V(\mathbf{r})$). A MESP minimum has three positive eigenvalues, represented as (3, +3) CP. A maximum has three negative eigenvalues ((3, −3) CP). Between the two types of saddle points, the CP with two negative and one positive curvatures is called a (3, −1) CP and the other with one negative and two positive curvatures is called a (3, +1) CP. Local maxima are always identified at the nuclear positions,[28] and so they do not provide any valuable chemical information. However, the positions and values of MESP minima that occur typically 1−2 Å away from the molecular frameworks are very important for judging the reactivity of the molecule.[27]

Table 1. C_{ipso}−Cr and C_{para}−Cr Bond Lengths (Å) of (substituted arene)$Cr(CO)_3$ Complexes at the HF/6-311G and B3LYP/6-311G (in italics) Levels of Theory

	substituent							
	NH_2	OH	CH_3	F	CHO	CN	NO_2	H
C_{ipso}−Cr	2.435	2.369	2.360	2.308	2.234	2.217	2.144	2.317
(se)[a]	*2.408*	*2.329*	*2.299*	*2.266*	*2.252*	*2.263*	*2.226*	*2.266*
C_{para}−Cr	2.325	2.320	2.331	2.312	2.289	2.282	2.240	2.330
(se)	*2.273*	*2.274*	*2.285*	*2.276*	*2.283*	*2.282*	*2.281*	*2.285*
C_{ipso}−Cr	2.410	2.363	2.354	2.317	2.268	2.269	2.208	2.330
(ae)[a]	*2.383*	*2.325*	*2.304*	*2.281*	*2.273*	*2.277*	*2.253*	*2.285*
C_{para}−Cr	2.353	2.346	2.336	2.331	2.224	2.223	2.171	2.317
(ae)	*2.280*	*2.276*	*2.274*	*2.266*	*2.260*	*2.260*	*2.255*	*2.266*

[a] Abbreviations: se, syn eclipsed; ae, anti eclipsed.

In electron density topography, a (3, −1) CP is the most important entity to describe the atoms in a molecule concept.[16] This CP is generally called a bond CP (BCP) since the gradient path of ρ (it is a curve such that the gradient vector $\nabla\rho$ is tangent to it in every point except when $\nabla\rho = 0$) originating from this point always terminates at a nucleus. According to Bader,[16] the necessary and sufficient condition for two atoms to be bonded is the presence of a bond path between them. In this work, the bonding between the aromatic ring and chromium atom is judged by locating the BCPs.

Results and Discussion

(a) Geometries and SCF Energies. In Table 1, the C_{ipso}−Cr and C_{para}−Cr bond lengths are given for syn-eclipsed and anti-eclipsed conformations of all the systems at HF/6-311G and B3LYP/6-311G levels. Vibrational frequencies of all the systems have been calculated only at the HF level, and they showed that, except for the anti-eclipsed $(C_6H_5NH_2)Cr(CO)_3$ and $(C_6H_5OH)Cr(CO)_3$ and syn-eclipsed $(C_6H_5CHO)Cr(CO)_3$ systems, all the other systems are energy minima. Since we have syn-eclipsed and anti-eclipsed conformations for all the complexes at the B3LYP level as well, it is expected that at least the most stable conformations are also energy minima in the B3LYP-level calculations. For example, the B3LYP/6-311G vibrational frequencies of the most stable conformations of $(C_6H_6)Cr(CO)_3$, $(C_6H_5NH_2)Cr(CO)_3$, and $(C_6H_5NO_2)Cr(CO)_3$ are all positive. In Table 2, the SCF energy differences between the syn-eclipsed and anti-eclipsed conformations at the HF/6-311G and B3LYP/6-311G levels are also given. The following

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Table 2. SCF Energy Difference (ΔE) between Syn-Eclipsed and Anti-Eclipsed Conformations ($E_{syn} - E_{anti}$) of (substituted arene)Cr(CO)$_3$ Complexes at HF/6-311G and B3LYP/6-311G (in italics) Levels

	substituent							
	NH_2	OH	CH_3	F	CHO	CN	NO_2	H
ΔE (kcal/mol)	−4.20	−2.91	−1.20	−2.07	2.58	1.25	2.33	0.00
	−3.42	*−3.67*	*−2.13*	*−1.74*	*1.82*	*1.55*	*3.76*	*0.00*

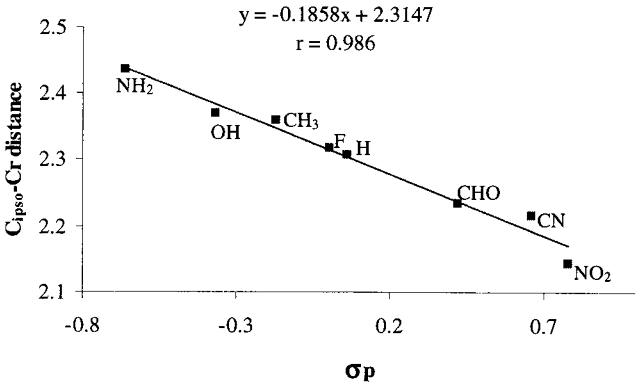

Figure 2. σ_p versus C_{ipso}−Cr distances (in Å) in syn-eclipsed conformations of (X-C_6H_5)Cr(CO)$_3$ at the HF/6-311G level.

conclusions can be drawn from these tables. Optimized geometries of all the syn-eclipsed systems with electron-donating groups have a longer C_{ipso}−Cr bond as compared to the corresponding C_{para}−Cr bond. The pattern is reversed in the case of an electron-accepting group. This observation holds good for the crystal structures as well.[3,29] On the other hand, in the case of anti-eclipsed conformations, C_{ipso}−Cr and C_{para}−Cr bonds show almost a uniform trend, with the former being longer. Interestingly, a good linear correlation with correlation coefficient (cc) equal to 0.973 is obtained by plotting the C_{ipso}−Cr distances of the most stable conformations of each complexes at the HF/6-311G level against the Hammett σ_p constants of the arene substituent (cf. Figure 2). Note that Hammett constants give a quantitative measure of the electron-donating or -withdrawing capacity of an arene substituent. A negative value indicates electron donation to the arene ring, and a positive value means electron withdrawal from the arene ring by the substituent.[14] In the present correlation, the C_{ipso}−Cr distance decreases with respect to an increase in the value of σ_p constants, suggesting that the strength of the interaction between the arene moiety and the chromium moiety is very much related to the electron-accepting/-releasing nature of the arene substituent. However, a similar correlation at the B3LYP level holds good only for systems with NH_2, OH, CH_3, F, and H as substituents (cc = 0.988). The electron-withdrawing groups NO_2, CN, and CHO do not fall on such a correlation graph (their inclusion gives cc = 0.807).

Table 3. MESP Values at the (3, +3) CPs (in au) of Syn-Eclipsed Conformations of (substituted arene)Cr(CO)$_3$ Complexes at HF/6-311G and B3LYP/6-311G (in italics) Levels[a]

substituent	CPs over arene ring	Cr(CO)$_3$ oxygen CPs			substit CPs
		O1	O2	O3	
H	0.0042	−0.0643	−0.0643	−0.0643	
	0.0089	*−0.0598*	*−0.0598*	*−0.0598*	
NH_2	−0.0033 (o) −0.0038 (p)	−0.0702	−0.0652	−0.0652	−0.0398
	0.0027 (p)	*−0.0629*	*−0.0677*	*−0.0677*	*−0.0206*
OH	0.0015 (o) 0.0035 (p)	−0.0665	−0.0606	−0.0603	−0.0808
	nil	*−0.0698*	*−0.0654*	*−0.0637*	*−0.0771*
CH_3	0.0030 (o) 0.0024 (p)	−0.0674	−0.0650	−0.0650	
	0.0083 (p)	*−0.0611*	*−0.0619*	*−0.0619*	
F	0.0100 (p)	−0.0624	−0.055	−0.0558	−0.0385
	nil	*−0.0570*	*−0.0545*	*−0.0545*	*−0.0286*
CHO	0.0019 (o) 0.0028 (p)	−0.0473	−0.0518	−0.0473	−0.0996
		−0.0508	*−0.0544*	*−0.0510*	*−0.0740*
CN	0.0066 (p)	−0.0470	−0.0464	−0.0464	−0.0943
	nil	*−0.0540*	*−0.0485*	*−0.0486*	*−0.0759*
NO_2	−0.0029 (o) −0.0030 (p)	−0.0348	−0.0245	−0.0245	−0.1022
	nil	*−0.0520*	*−0.0444*	*−0.0449*	*−0.0613*

[a] See text and Figure 1 for details. The labels “o”, “p” and “m” represent the ortho, para, and meta positions of the arene ring.

The SCF energies (cf. Table 2) are in good agreement with what is normally observed for the stable conformations of these systems: all the conventional ortho−para-directing groups (NH_2, OH, CH_3, F) prefer syn-eclipsed conformations, and all the electron-withdrawing groups (CHO, CN, NO_2) prefer anti-eclipsed conformations[5,29] at both the HF and B3LYP levels of theory. However, the eclipsed structure of the (unsubstituted arene)Cr(CO)$_3$ complex is found to be slightly more stable than its staggered conformation at the HF and B3LYP levels (in the crystal state, the latter is the preferred structure[30,31]). The eclipsed conformation of (arene)Cr(CO)$_3$ is useful in order to make a direct comparison with other (substituted arene)Cr(CO)$_3$ systems. It can be noted from Tables 1 and 2 that the HF and B3LYP results give very similar trends for both the geometric and energetic parameters of these systems. However, the inclusion of correlation via the B3LYP functional gives a tighter binding between the arene and the chromium carbonyl moiety, as indicated by the shorter C−Cr bonds in comparison to HF/6-311G values.

(b) MESP and Electron Density Topography. In Tables 3 and 4, MESP minima observed over the arene ring (they are near ortho, meta, and para carbon atoms), near each Cr(CO)$_3$ oxygen atom (these appear around 1.25−1.37 Å away from the carbonyl oxygen along its bond direction), and near the substituent (these are generally due to the lone pair electrons of the substituent) are depicted as HF/6-311G and B3LYP/6-311G level

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(29) (a) Meurs, F. V.; Koningsveld, H. V. *J. Organomet. Chem*, **1977**, *131*, 423. (b) Saillard, J. Y.; Grandjean, D. *Acta Crystallogr.* **1976**, *B32*, 2285. (c) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 228. (d) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem.Soc. A* **1967**, 1619. (e) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27. (f) Schollkopf, K.; Stezowski, J. J.; Effenberger, F. *Organometallics* **1985**, *4*, 922.

(30) The experimental geometry of $C_6H_6Cr(CO)_3$ (staggered form) can be seen in: (a) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314. (b) Rees, B.; Coppens, P. *J. Organomet. Chem.* **1972**, *42*, C102. Rees and Coppen were the first to suggest a trigonally prismatic coordination for Cr in this complex by considering Cr as preferentially bonded to the C−C bonds that are eclipsing the CO groups (in this paper, a trigonally prismatic structure corresponds to the staggered conformation).

(31) For extended Hückel calculations on metal carbonyls, see: Albright, T. A.; Yee, K. A.; Saillard, J. Y.; Kahlal, S.; Halet, J.-F.; Leigh, J.-S.; Whitmire, K. H. *Inorg. Chem.* **1991**, *30*, 1179.

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Table 4. MESP Values at (3, +3) CPs (in au) of Anti-Eclipsed Conformations of (substituted arene)$Cr(CO)_3$ Complexes at HF/6-311G and B3LYP/6-311G (in itallics) Levels[a]

substituent	CPs over arene ring	$Cr(CO)_3$ oxygen CPs O1	O2	O3	substit CPs
H	0.0042	−0.0643	−0.0643	−0.0643	
	0.0089	*−0.0598*	*−0.0598*	*−0.0598*	
NH_2	−0.0025 (m)	−0.0726	−0.0637	−0.0662	−0.0414
	0.0042 (m)	*−0.0662*	*−0.0666*	*−0.0666*	*−0.0259*
OH	0.0038 (m)	−0.0614	−0.0667	−0.0603	−0.0796
	nil	*−0.0585*	*−0.0618*	*−0.0593*	*−0.0604*
CH_3	0.0028 (m)	−0.0679	−0.0650	−0.0650	
	0.0081 (m)	*−0.0612*	*−0.0614*	*−0.0614*	
F	0.0105 (m)	−0.0608	−0.0563	−0.0563	−0.0377
	nil	*−0.0536*	*−0.0562*	*−0.0562*	*−0.0232*
CHO	nil	−0.0469	−0.0410	−0.0498	−0.1099
	nil	*−0.0494*	*−0.0525*	*−0.0500*	*−0.0803*
CN	nil	−0.0405	−0.0479	−0.0479	−0.0990
	nil	*−0.0476*	*−0.0492*	*−0.0492*	*−0.0793*
NO_2	−0.0013 (o)	−0.0241	−0.0289	−0.0289	−0.1083
	nil	*−0.0433*	*−0.0454*	*−0.0454*	*−0.0674*

[a] See text and Figure 1 for details. The labels "o" and "m" represent the ortho and meta positions of the arene ring.

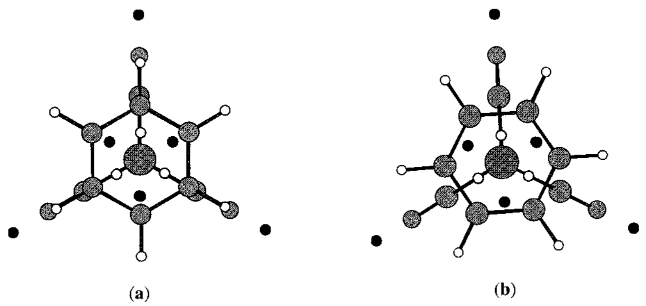
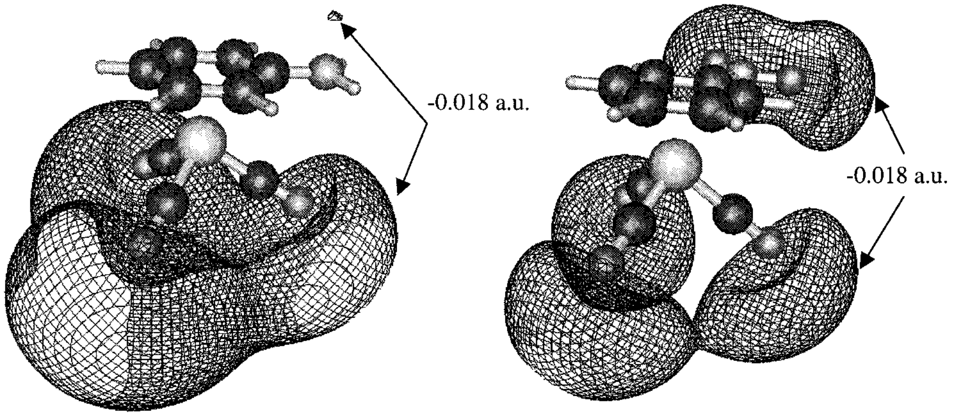

(a) (b)

Figure 3. Top view of (a) eclipsed and (b) staggered conformations of (benzene)$Cr(CO)_3$. Small circles inside the ring and near the oxygen atoms are MESP CPs (black and white dots are (3, +3) and (3, +1) CPs, respectively).

geometries. At the HF/6-311G level, the eclipsed form of (benzene)$Cr(CO)_3$ has three (3, +3) CPs which appear over the ring carbon atoms that are anti with respect to the CO groups (C_{anti}). These are connected via three (3, +1) CPs located above the ring carbons that are syn with respect to the CO groups (C_{syn}). In the case of the staggered form of (benzene)$Cr(CO)_3$, the (3, +3) CPs appear above the midpoint region of the C−C bonds. However, the staggered form is not a local minimum. Both cases are depicted in Figure 3. Note that all the ring CPs possess positive values. However, at the B3LYP/6-311G level, no MESP minimum is located over the arene ring. It is interesting to compare these topographies with that of free benzene. At the HF and B3LYP levels, benzene shows six (3, +3) CPs over the midpoint region of each C−C bond that are connected via six (3, +1) CPs over the ring carbon atoms.[32] The MESP value at each minimum is −0.0325 au at the HF/6-311G level and −0.0293 at the B3LYP/6-311G level. MESP values at the minima thus suggest that the complexation of benzene with $Cr(CO)_3$ drastically decreases the negative potential over the arene ring. This supports both the high electron-withdrawing capacity of the $Cr(CO)_3$ group and the high tendency of its arene counterpart toward nucleophilic reactions as compared to free systems. In fact, the positive character of MESP over the arene ring suggests that $Cr(CO)_3$ moiety is an even stronger electron-withdrawing group than the NO_2 group (nitrobenzene has a faint negative MESP over the arene ring).

The presence of electron-donating or -withdrawing groups only marginally changes the MESP over the arene ring as compared to free substituted benzene. For example, at the HF level the difference between the MESP value at the (3, +3) ring CP of (aniline)$Cr(CO)_3$ and (benzene)$Cr(CO)_3$ is only 0.0052 au. However, the electron-donating effect of one amino group increases the negative character of MESP by 0.02 au in an uncomplexed system. It is also noted that, in general, the region above the arene ring of the complexes show only positive values for the MESP. Exceptions are the results obtained at the HF level for NH_2 and NO_2 as substituents. However, it can be noted that the negative potential at the $Cr(CO)_3$ oxygen minima varies, depending on the nature of the arene substituent. It is increased with an electron-donating substituent and decreased with an electron-accepting substituent (cf. Figure 4 for an illustration). The extreme cases of the electron donation and withdrawal effects are observed in complexed aniline and complexed nitrobenzene, respectively. In comparison to the HF results, the



(a) (b)

Figure 4. MESP isocontours of value −0.018 au at the B3LYP/6-311G level showing the substituent effects: (a) $(C_6H_5NH_2)Cr(CO)_3$; (b) $(C_6H_5NO_2)Cr(CO)_3$.

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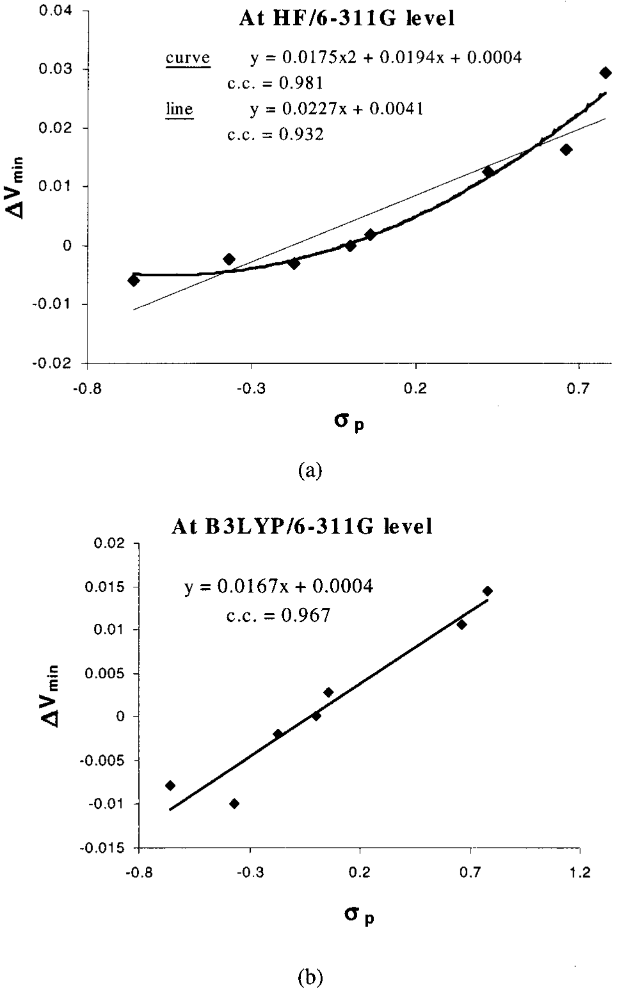

Figure 5. Relation between MESP minima at the carbonyl oxygen and Hammett σ_p constants at the (a, top) HF/6-311G and (b, bottom) B3LYP/6-311G levels.

Table 5. C_{ipso}−Cr and C_{para}−Cr Bond Lengths (Å) of (Substituted arene)chromium Carbonyl Complexes at HF/Gen, B3LYP/Gen, MP2/6-311G, and MP2/Gen Levels

	C_{ipso}−Cr, C_{para}−Cr			
substit[a]	HF/Gen	B3LYP/Gen	MP2/6-311G	MP2/Gen
H	2.255, 2.269	2.227, 2.246	2.201, 2.230	2.168, 2.191
NH_2 (se)	2.363, 2.269	2.336, 2.242	2.267, 2.207	2.233, 2.175
OH (se)	2.333, 2.270	2.298, 2.240	2.210, 2.216	2.205, 2.180
NO_2 (ae)	2.176, 2.142	2.218, 2.221	2.216, 2.219	2.155, 2.186

[a] Abbreviations: se, syn eclipsed; ae, anti eclipsed.

B3LYP results in general show a decrease in the negative character of the MESP at all the CPs. One exception is the syn-eclipsed conformation of the OH-substituted system, wherein the oxygen and the arene ring CPs have more negative character than the Hartree−Fock value. As compared to the HF-level topography, the B3LYP-level topography does not show MESP minima over the arene ring in most of the cases. This is probably due to the overall decrease in the negative character of the MESP at the B3LYP level.

We have also noted a correlation between the carbonyl stretching frequencies obtained at the HF level and the nature of the arene substituent. For the unsubstituted complex, the minimum and maximum CO stretching frequencies are 2028 and 2127 cm^{-1}, respectively. When the arene ring has an electron-withdrawing susbtituent, the CO frequencies increase from this value. These increase for the minimum and maximum values of F-, CHO-, CN-, and NO_2-substituted systems are (+16, +8), (+66, +30), (+69, +24), and (+152, +88) cm^{-1}, respectively. On the other hand, the (minimum, maximum) values of the CO frequencies of NH_2-, OH-, and CH_3-substituted systems show a slight decrease of (+9, +8), (+11, −1), and (+9, +7) cm^{-1}, respectively, from the corresponding CO frequencies of $(C_6H_6)Cr(CO)_3$. However, we note here that the CO frequencies are known to be very sensitive to the back-bonding, which is poorly represented at the HF level, and this could be the reason for the strong influence of the electron-withdrawing groups or the weak influence of the electron-donating groups on the CO stretching frequencies.[33] To understand this behavior, we have calculated the CO stretching frequencies of the unsubstituted and NO_2- and NH_2-substituted (arene)Cr(CO)$_3$ complexes at the B3LYP/6-311G level as well. The respective CO frequencies in the order (minimum, maximum) in cm^{-1} are (1859, 1917), (1879, 1935), and (1843, 1907). In comparison to the HF-level frequencies, these frequencies show an ∼10% reduction in their values. Among the B3LYP-level CO stretching frequencies, the values of NO_2- and NH_2-substituted systems show only a moderate increase and decrease, respectively, from the corresponding values of the unsubstituted arene complex. Considering the DFT results as more reliable, it can be concluded that at the HF level the CO stretching frequencies are overestimated for the systems with electron-withdrawing groups in comparison to the systems with electron-donating groups.

Since the electron-accepting/-releasing nature of the substituent is greatly reflected in the MESP values of the carbonyl oxygen CPs, a correlation between the values of the MESP at these CPs and Hammett σ constants is expected. To obtain this correlation, the most negative carbonyl oxygen CP corresponding to the most stable structure of the complex is selected (defined here as V_{min}). The substituent effect on MESP is quantified in terms of the difference between the V_{min} value of the substituted system with the V_{min} value of the unsubstituted system. This quantity is defined as ΔV_{min}. In Figure 5, ΔV_{min} values obtained at the HF and B3LYP levels are plotted against Hammett σ_p constants. It can be noted that at the HF level a curve fitting is better than a line fitting. The fitted curve suggests a higher rate of increase in the ΔV_{min} value when the substituent is becoming more and more electron withdrawing. However, the B3LYP-level diagram gives a good linear correlation. Thus, a comparison of the two diagrams points out that the correlation effects are more important in systems with strong electron-withdrawing groups than in systems with electron-releasing groups.

Yet another interesting feature mainly observed at the HF-level topography is that, in all the syn-eclipsed conformations, the MESP minima appear near either para or both ortho and para carbon atoms (cf. Figure 1) and all the anti-eclipsed conformations except the one

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(32) Boutonnet, J. C.; Mordenti, L.; Rose, E.; Precigoux, G. *J. Organomet. Chem.* **1981**, *221*, 147 and references therein. (b) Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 955.

(33) This was pointed out by one of the reviewers.

Table 6. MESP Values at the (3, +3) CPs (in au) of (substituted arene)$Cr(CO)_3$ Complexes at (1) HF/Gen, (2) B3LYP/Gen, (3) MP2/6-311G, and (4) MP2/Gen Levels[a]

substit	level	CPs over arene ring	$Cr(CO)_3$ oxygen CPs			substit CPs
			O1	O2	O3	
H	1	−0.0060	−0.0420	−0.0420	−0.0420	
2	0.0042	−0.0437	−0.0437	−0.0437		
3	nil	−0.0620	−0.0620	−0.0620		
4	nil	−0.0522	−0.0522	−0.0522		
NH_2	1	−0.0084 (p)	−0.0482	−0.0482	−0.0522	−0.0338
(se)		−0.0081 (o)				
2	−0.0003 (o)	−0.0437	−0.0437	−0.0487	−0.0490	
−0.0009 (p)						
3	0.0096 (p)	−0.0592	−0.0740	−0.0740	−0.0481	
4	nil	−0.0492	−0.0624	−0.0624	−0.0527	
OH	1	−0.0097 (o)	−0.0378	−0.0387	−0.0392	−0.0551
(se)		−0.0083 (p)				
2	0.0044 (o)	−0.0439	−0.0453	−0.0459	−0.0388	
0.0042 (p)						
3	nil	−0.0560	−0.0633	−0.0633	−0.0590	
4	0.0120 (p)	−0.0472	−0.0565	−0.0565	−0.0355	
NO_2	1	−0.0087 (p)	−0.0105	−0.0153	−0.0153	−0.0936
(ae)		−0.0090 (m)				
2	nil	−0.0295	−0.0321	−0.0321	−0.5960	
3	nil	−0.0514	−0.0454	−0.0454	−0.0537	
4	nil	−0.0454	−0.0371	−0.0371	−0.0507	

[a] See text and Figure 1 for details. The labels "o", "p", and "m" represent the ortho, para, and meta positions of the arene ring. Abbreviations: se, syn eclipsed; ae, anti eclipsed.

with the NO_2 group show the MESP minima near the meta carbon atoms. In other words, all the systems studied here except one (NO_2-substituted system) always show the MESP minima near C_{anti} at the HF level. This means that C_{anti} atoms are more electron-rich as compared to C_{syn} atoms. Thus, irrespective of the substituent and the conformation of the complex, an electrophile would prefer to attack a C_{anti} atom and a nucleophile would prefer to attack C_{syn} positions.[2a,32,34] This particular feature was reported by Jackson et al.[30] for the reactions leading to the stereoelectronic control of the regioselectivity of both electrophilic and nucleophilic substitution of (η^6-1,1-dimethylindane)tricarbonylchromium.

Further evidence to this fact is obtained from analyzing the bond critical points of the electron density topography located in the region between the chromium atom and the arene ring. The most important observation is that, irrespective of the level of theory (HF or B3LYP) used, almost all the arene systems (both syn- and anti-eclipsed conformations) showed a (3, −1) bond CP between the C_{syn} atom and the chromium atom. In Figure 1, this feature is depicted wherein the bonds from the metal to arene ring are drawn based on the BCP location. Thus, this electron density topographical analysis suggests a trigonal-prismatic structure[30] for all the complexes studied here. One exception to this observation is the NO_2-substituted system at the HF level, where the C_{ipso} and the C_{para} carbons are connected to the metal atom via a (3, −1) bond CP. We have also compared the electron density and the ellipticity values of the BCPs at the HF and B3LYP levels. The electron density is almost same at both levels (the ratio being ~1). However, the ratio of the HF to B3LYP ellipticity values ranges from 0.4 to 3.4.

We have also studied the MESP topography of selected systems (only the most stable conformation) at the MP2/6-311G level as well as used a general basis containing extra polarization functions for heavy elements other than chromium at the HF, B3LYP, and MP2 levels. Some geometric parameters and MESP topography results obtained at these levels are given in Tables 5 and 6, respectively. A comparison of Tables 1 and 5 shows a shortening of the chromium to arene carbon distances at the higher level calculations. As compared to the B3LYP geometries, the MP2 geometries show a greater amount of bond shortening. A general observation is that the inclusion of the extra polarization functions in the basis set decreases the overall negative character of the MESP in every system. MP2 results are somewhat similar to the B3LYP results. However, some discrepancies can be noticed. For example, in the case of (aniline)$Cr(CO)_3$, the MESP minimum corresponding to the O3 atom is more negative than O1 and O2 at the B3LYP level. However, this order is reversed at MP2-level topography. A similar observation is seen in the (nitrobenzene)$Cr(CO)_3$ system as well.

Concluding Remarks

The MESP topography obtained at all the levels of calculations suggests that the arene ring in every system is highly deactivated, due to the complexation of it with the chromium moiety. However, depending on the nature of the substituent, significant changes are observed in the MESP surrounding the carbonyl oxygen (cf. Figure 5). These changes at the B3LYP level show good linear correlation with the Hammett σ_p constants. The density topography unambiguously characterizes the complexes as having a trigonally prismatic structure, since only the C_{syn} carbon atoms are connected via a bond CP to the chromium atom. In general, the strength of the complexation, the overall geometry of the complex, and the electron-accepting power of the $Cr(CO)_3$ moiety are intimately connected with the electron-accepting/-releasing nature of the arene substituent.

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(34) Jackson, W. R.; Rae, I. D.; Wong, M. G.; Semmelhack, M. F.; Garcia, J. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1359.

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