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Electron Redistribution of Aromatic Ligands in (Arene)Cr(CO)$_3$ Complexes. Structural (Bond-Length) Changes as Quantitative Measures

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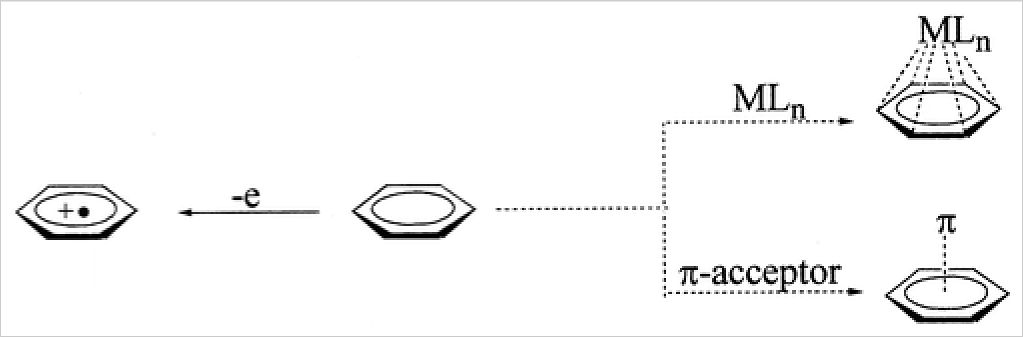
Synopsis

Structural changes of arene ligands upon coordination with Cr(CO)$_3$ result from charge transfer, and they are shown to be quite similar to those found in π-complexes with NO$^+$ and arene cation radicals.

Abstract



Arene ligands experience significant ring expansion upon coordination with chromium tricarbonyl, as established by precise X-ray crystallographic analyses of various (η^6-arene)$Cr(CO)_3$complexes. Such changes in ligand structures result from the charge (electron) redistribution, Ar^+–Cr^-, upon arene coordination, since they are closely related to those found in the intermolecular 1:1 complexes of the corresponding series of arenes with nitrosonium cation (NO^+). The latter are prototypical examples of charge-transfer complexes as described by Mulliken. As such, they show enhanced degrees of charge (electron) transfer that approach unity, which is confirmed by quantitative comparison with the structural changes measured in the one-electron (oxidative) transformation of electron-rich arene donors (Ar) to the cation-radicals ($Ar^{\bullet+}$). Such a charge redistribution thus readily accounts for the enhanced reactivity to nucleophilic attack of the arene ligand in various $ArCr(CO)_3$ complexes and related transition-metal/arene analogues.

Introduction

Chromium tricarbonyl complexes with various arene ligands are finding increasing use in organic synthesis.[1,2] Critical to this application is an understanding as to how complexation by chromium tricarbonyl affects the aromatic ligand itself. Heretofore, most of the theoretical attention has been directed toward an understanding of the bonding of $Cr(CO)_3$ to the arene.[3] Although there are numerous reports on the X-ray crystallographic characterization of (η^6-arene)$Cr(CO)_3$ complexes, only a few of them address the bond-length changes in the arene companion upon coordination with $Cr(CO)_3$.[4] The latter must be an important factor since it has been found that $Cr(CO)_3$ confers upon the η^6-coordinated arene a higher activity and a greater susceptibility to nucleophilic substitution with concomitant reduced reactivity to electrophilic attack.[5] A substantial dipole moment ($\mu \approx 5$ D) has been measured in the benzene complex (η^6-C_6H_6)$Cr(CO)_3$ which increases with the number of electron-donating substituents and decreases with electron-withdrawing substituents, as expected for an overall bond moment in the direction (arene) → (Cr).[6] These observations lead to the notion that the multicentered ligand-to-metal bond in tricarbonylchromium complexes involves the transfer of electron density from the arene π-orbitals to the 3d-orbitals of the transition-metal center. Indeed, the electrochemical reduction of (η^6-arene)$Cr(CO)_3$ complexes is generally much easier than that of the free (uncomplexed) arene, qualitatively indicating electron removal from the arene ligand.[7,8] On the other hand, the first ionization potential (involving electron ejection from the chromium 3d- orbital) greatly decreases from IP = 8.40 eV in $Cr(CO)_6$[9] to 7.42 eV in (η^6-C_6H_6)$Cr(CO)_3$,[10] i.e., upon the replacement of a weak donor ligand by a stronger (benzene) donor.

Earlier, Pauling proposed a direct relationship between the length of a chemical bond and its electron population or bond order,[11] i.e.,

$$d_{\mathrm{N}} = d_1 - 0.6 \log N \qquad (1)$$

where d_{N} is the length of a particular bond with bond order N, and d_1 is the length of the corresponding single bond. [Note that the number of bonding electrons is $n = 2N$.] As such, bond-length measurements can provide a quantitative guide to the electron-density distribution. For our purposes here, the electron redistribution of the arene ligand upon complexation can be obtained by a precise comparison of its bond-length changes relative to that extant in the free (uncomplexed) donor. To examine this problem, we focused in Chart 1 on two classes of electron-rich arenes, as measured by their oxidation potentials of $E°_{\mathrm{ox}} < 1.6$ V vs SCE.[12]

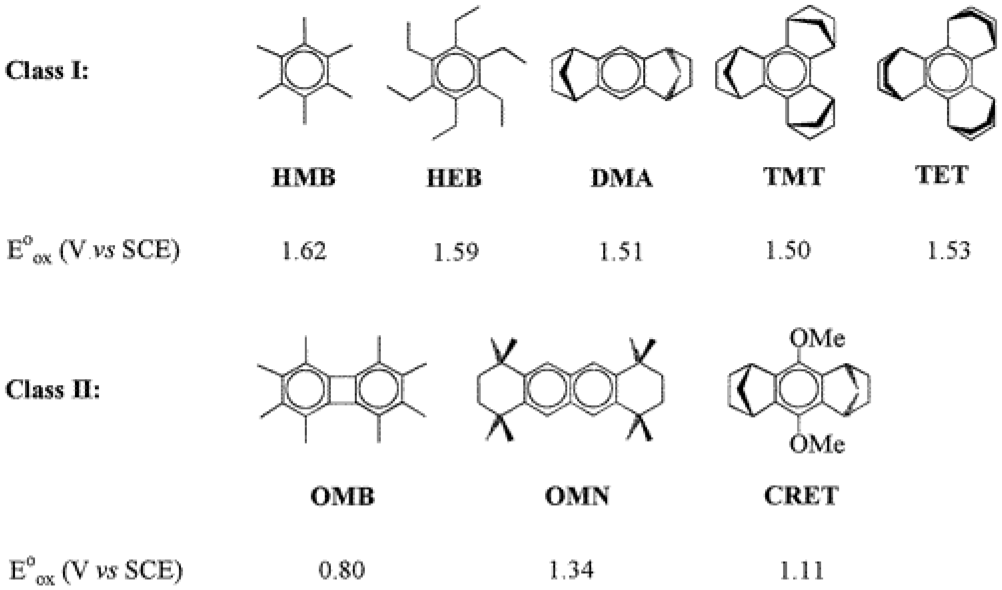


Chart 1

The arene donors in class I are highly alkylated benzenes of more or less the same donor strengths, as measured by their reversible oxidation potentials $E°_{\mathrm{ox}}$.[13] Class II donors are electron-rich polycyclic aromatics with rather low oxidation potentials ($E°_{\mathrm{ox}} < 1.34$ V).[14]

Results and Discussion

The chromium tricarbonyl complexes of the aromatic donors in Chart 1 were prepared according to the method of Mahaffy and Pauson,[15] i.e.,

$$\text{arene} + \mathrm{Cr(CO)_6} \rightarrow \text{(arene)}\mathrm{Cr(CO)_3} + 3\mathrm{CO} \qquad (2)$$

Single crystals of the (arene)$\mathrm{Cr(CO)_3}$ complexes were mounted for X-ray crystallographic analysis at −150 °C, unless specified otherwise. As a comparative basis, X-ray crystal structures of the free (uncomplexed) aromatic donor were determined under the same conditions, or the structural data were retrieved from the Cambridge Crystallographic Database.[16]

1. Structural Changes of Class I Aromatic Donors in Tricarbonylchromium Complexes. The molecular structures of the 1:1 complexes of $Cr(CO)_3$ and class I arene donors adopt the usual staggered conformation, with Cr lying above the benzenoid ring (equidistant from each ring carbon), as illustrated in the top perspectives for **HMB** and **TET** in Figure 1. The distance between chromium and the center of the benzenoid ring in the **HMB** complex is 1.731(3) Å, but it is longer in the hindered **TET** (1.753 Å) and **DMA** (1.770 Å) analogues, the faces of which are shielded by bicyclic substituents against the approach of $Cr(CO)_3$.[17]

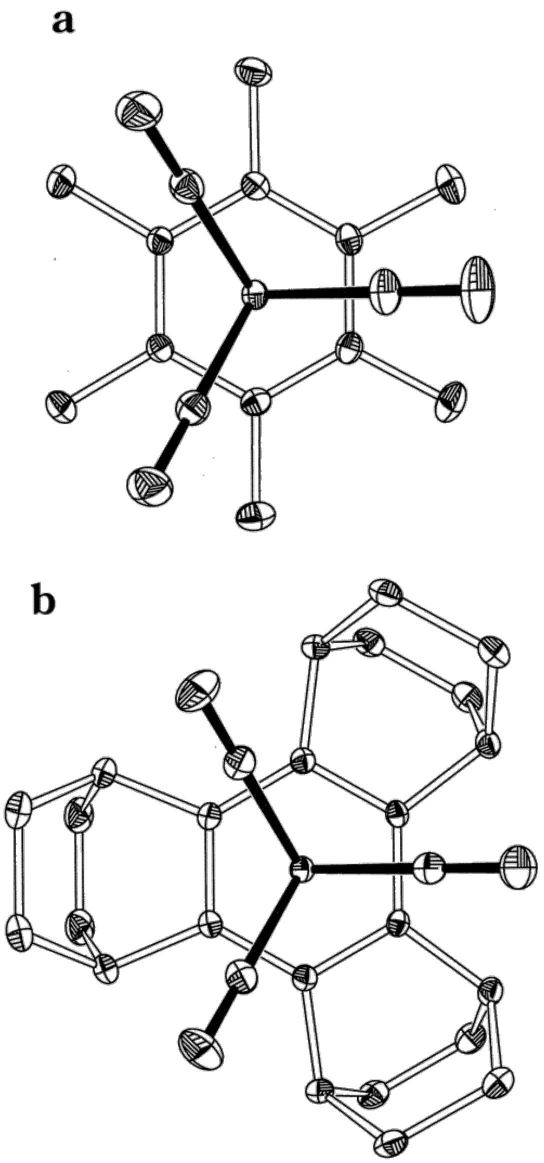
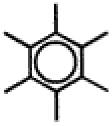
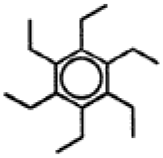
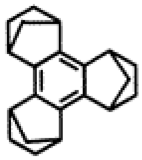
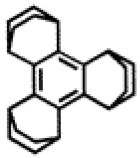
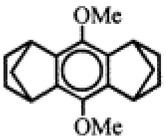


Figure 1 Molecular structures (top perspective) of typical (arene)$Cr(CO)_3$ complexes where arene = **HMB** (a) and **TET** (b) as described in Chart 1. Hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability level.

The expansion of the benzenoid ligand upon complexation is the structural feature that we consider most important in this study. As such, Table 1 reports the average aromatic (C−C) bond distance (*d*) in the complexed aromatic ligand relative to that in the free arene donor.[18,19] Most importantly, the notable increase in the average C−C bond lengths of Δ = 1.0−1.9 pm is observed in all cases and establishes the *significant expansion of the aromatic ligand* upon $Cr(CO)_3$coordination.

Table 1. Average C−C Bond Length (Å) within the Aromatic Rings of Substituted Monocyclic Arenes in the Neutral Donors and upon Complexation with $Cr(CO)_3$ and NO^+(Values in Bold Indicate the Bond Length Changes (Δ) Relative to the Neutral Donor)

	Arene	Uncomplexed Donor	$Cr(CO)_3$ Complex	NO^+ Complex
HMB		1.411(1)	1.426(1) **+1.5 pm**	1.415(2) **+0.4 pm**[a]
HEB		1.402(2)[b]	1.421(5)[c] **+1.9 pm**	1.417(3)[d] **+1.4 pm**
DMA		1.399(3)	1.409(4) **+1.0 pm**	1.409(2) **+1.0 pm**
TMT		1.401(1)[e]		1.411(5) **+1.0 pm**
TET		1.401(1)	1.420(2) **+1.9 pm**	1.414(2)[d] **+1.3 pm**
CRET		1.398(1)	1.416(3) **+1.8 pm**	1.412(4) **+1.4 pm**

[a] See ref 40.[b] From ref 16a.[c] From ref 16c.[d] From ref 26.[e] From ref 16.

2. Structural Changes of Class I Aromatic Donors in Charge-Transfer Complexes with Nitrosonium Cation. To place the structural alteration of the arene ligand in perspective, let us compare the change in arene structure when it is involved in the intermolecular noncovalent interaction with a bona fide electron acceptor such as nitrosonium (NO^+),[20] e.g., where X^- = BF_4^-, $SbCl_6^-$, $AlCl_4^-$, etc. The nitrosonium complexation in eq 3 is kinetically reversible, and the results in Table 2 show that the formation constants K_{EDA} for the class I donors are uniformly high in acetonitrile solutions. Table 2 also includes the absorption maximum of the diagnostic (UV–vis) absorption band (λ_{CT}) of the arene/NO^+ complexes.[21]

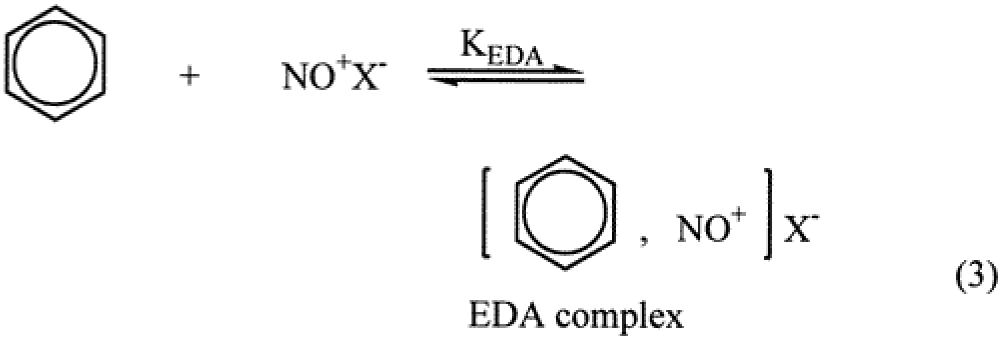


Table 2. Donor/Acceptor Association of Hexaalkylbenzenes with Nitrosonium Tetrafluoroborate[a]

donor	λ_{CT} (nm)	K_{EDA} (M^{-1})	ε_{CT} (M^{-1} cm^{-1})
HMB	337	31 000	3100
CRET	350	28 000	*b*
DMA	340	*b*	*b*
TMT	352	34 000	3500
TET	355	33 500	3400
HEB	347	32 500	2900

[a] In acetonitrile containing 1 mM $NOBF_4$ and 5–10 mM donor at 20 °C.[b] Not available.

X-ray crystallographic analysis of the various aromatic complexes with NO^+ has established the general π-character of the intermolecular interaction (Figure 2), which is indeed highly reminiscent of the symmetric (3-fold) structures of (arene)$Cr(CO)_3$ shown in Figure 1. However, the main-group acceptor (NO^+) can utilize only the limited 2s- and 2p-orbitals for π-bonding to the arene donor,[22] unlike the transition-metal moiety $Cr(CO)_3$, which has highly delocalized (multicenter) 3d-orbitals available for charge-transfer bonding. The spectral complexity of the latter can obscure the essential electron redistribution in the arene ligand. On the other hand, the various π-complexes of NO^+ and arene donors represent prototypical charge-transfer interactions. Most importantly, they are fully (and quantitatively) formulated by Mulliken theory,[23,24] which is particularly useful in the delineation of electron redistribution in intermolecular interactions (DA) between electron donors (D) and acceptors (A), i.e.,

$$\psi_{DA} = a\psi_{D,A} + b\psi_{D+A-} + \ldots \qquad (4)$$

where ψ_{DA} represents the wave function of the electron donor/acceptor complex, and $\psi_{D,A}$ and ψ_{D+A-} represent those of the van der Waals and the dative (charge-transfer) components, respectively. As such, the arene donor is subject to a delocalized (charge-transfer) perturbation by NO^+, the magnitude of which is given as a spectral shift of λ_{CT} and proportional to $E°_{ox}$.[25] With an electron-rich donor such as **HMB**, the degree of charge transfer is approximated by the (conceptual) structural change illustrated in eq 5, in which the donor moiety largely takes on the structure of the aromatic cation radical and the acceptor that of nitric oxide.[20,26]

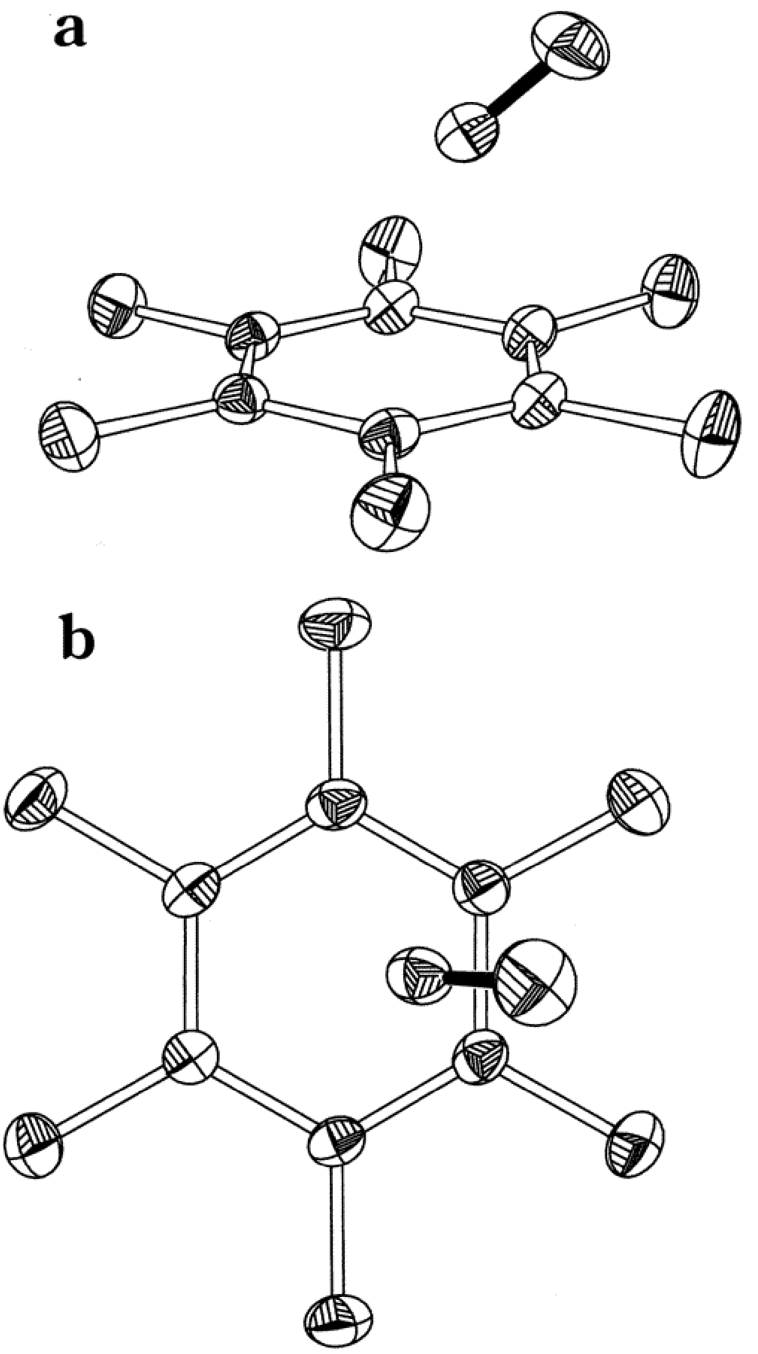
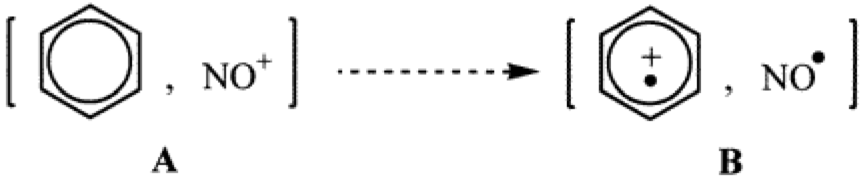


Figure 2 Charge-transfer complex of hexamethylbenzene (**HMB**) and NO^+ in 45° perspective (a) and top perspective (b). Hydrogens and $SbCl_6^-$ counterion omitted for clarity.



(5)

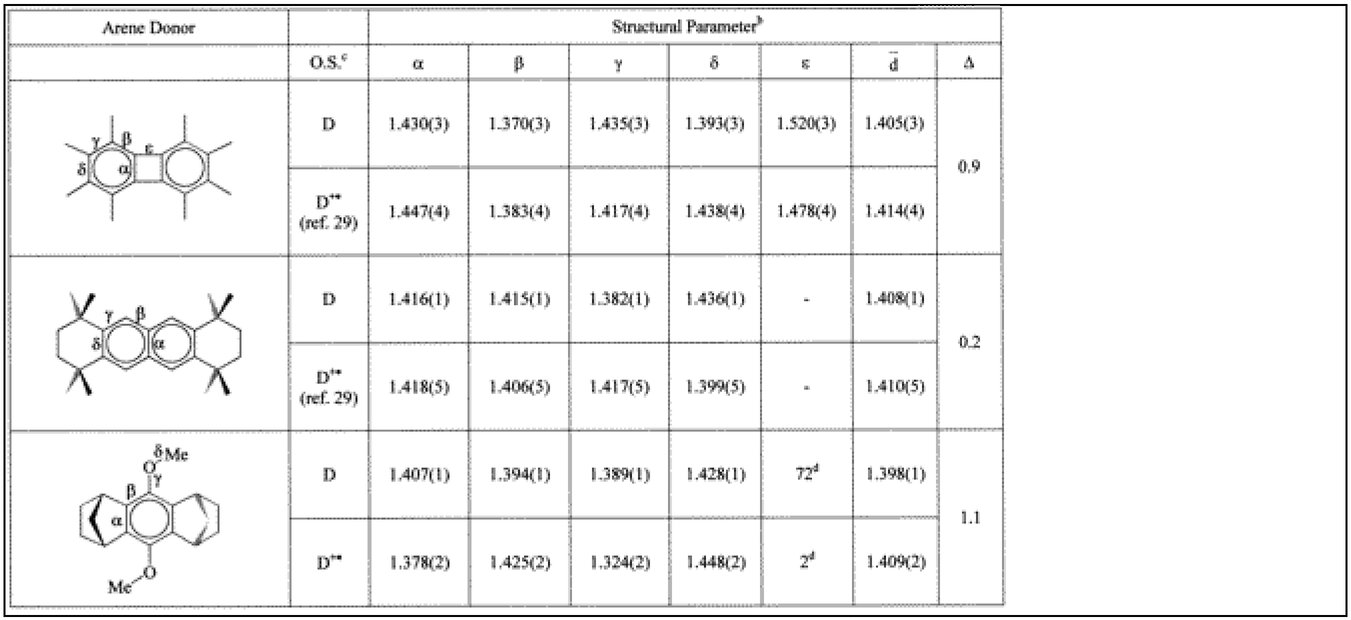
3. Comparative Ring Expansions of Arene Ligands upon $Cr(CO)_3$ and NO^+ Complexation. For comparison, the X-ray data for the (η^6-arene)$Cr(CO)_3$ complexes in Table 1 also include the structural changes of the arene donor when subjected to the "noncovalent" interaction with NO^+. It is noteworthy that the values of the structural changes, as denoted by Δ in the last column (bold type), are sizable and consistently similar to the Δ values for $Cr(CO)_3$ complexation. According to Pauling's bond-length/bond-order relationship in eq 1, the significant magnitudes of Δ in Table 1 point to the transfer of charge (electron) density from the aromatic donor to $Cr(CO)_3$ in amounts comparable to that with NO^+.[19]

To obtain a more quantitative measure of electron transference, we next turned to the class II arene donors in which the transfer of a full electron can be directly evaluated by comparing Δ in the formation of the aromatic cation radical itself, i.e.,

$$\text{arene} \xrightarrow{-e} \text{arene}^{\bullet+} \qquad (6)$$

4. Structural Changes in Aromatic Cation Radicals. As molecular entities, aromatic cation radicals are highly reactive, and those in class I are too transient to isolate as crystalline salts.[27] However, the multiring aromatic ligands in class II are better electron donors (with $E^\circ_{ox} < 1.3$ V vs SCE), and most importantly they yield substantially more persistent cation radicals, the salts of which can be isolated at low temperatures as single crystals suitable for X-ray diffraction analysis.[28] As such, Table 3 lists the important structural changes attendant upon the conversion of the class II donors **OMB**, **OMN**, and **CRET** to their cation radicals.

Table 3. Structural Changes of Class II Arene Donors Attendant upon One-Electron Oxidation to Their Cation Radicals[a]



Arene Donor		Structural Parameter[b]						
	O.S.[c]	α	β	γ	δ	ε	$\bar{d}$	Δ
	D	1.430(3)	1.370(3)	1.435(3)	1.393(3)	1.520(3)	1.405(3)	0.9
	$D^{\bullet+}$ (ref. 29)	1.447(4)	1.383(4)	1.417(4)	1.438(4)	1.478(4)	1.414(4)	
	D	1.416(1)	1.415(1)	1.382(1)	1.436(1)	-	1.408(1)	0.2
	$D^{\bullet+}$ (ref. 29)	1.418(5)	1.406(5)	1.417(5)	1.399(5)	-	1.410(5)	
	D	1.407(1)	1.394(1)	1.389(1)	1.428(1)	72[d]	1.398(1)	1.1
	$D^{\bullet+}$	1.378(2)	1.425(2)	1.324(2)	1.448(2)	2[d]	1.409(2)	

[a] All structures have a crystallographic center of symmetry.[b] In units of Å, except for Δ in pm, unless indicated otherwise.[c] O.S. is the oxidation state for the neutral donor (D) and its cation radical ($D^{\bullet+}$).[d] Dihedral angle between the benzene plane and the methoxy substituent in degrees.

The comparison of the interatomic bond lengths in neutral **OMB** with those in the cation radical **OMB**$^{\bullet+}$ in Table 3 reveals the average C−C bond length in the phenyl rings of **OMB**$^{\bullet+}$ to be 0.9 pm longer than that in the neutral donor, indicative of a significant ring expansion upon electron removal.[29]

The ring-expansion phenomenon is also observed in the cation radical of the encumbered hydroquinone ether **CRET**$^{\bullet+}$. Thus Table 3 shows that, upon one-electron oxidation, the average C−C bond length within the central aromatic ring of **CRET** increases substantially by 1.1 pm in the cation radical relative to that in the neutral precursor. In addition, upon oxidation the central ring in**CRET** suffers a quinoidal distortion and the peripheral OMe groups rotate into the aromatic plane (Figure 3). For convenience, the equivalent bonds in **CRET** are denoted by letters α, β, and γ in structure **C**.

C.

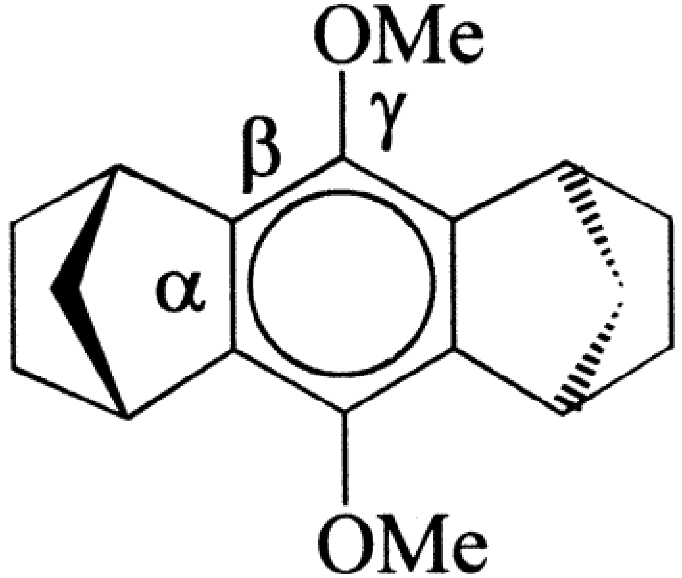
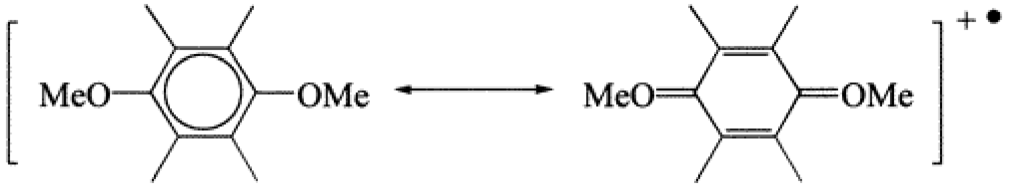


Table 3 shows that upon one-electron oxidation bonds α and γ become 2.9 and 6.5 pm shorter, respectively, whereas bond β becomes 3.1 pm longer, owing to a major contribution from the quinoidal structure **D**,[30] i.e.,



D.

The last structural feature in **CRET**$^{\bullet+}$ concerns the motion of the peripheral methoxy arms. As depicted in Figure 3, when the **CRET** molecule is oxidized, the OMe arms rotate until they lie in the plane of the central ring (torsion angle C−C−O−Me is 2°), whereas they are perpendicular to this plane in neutral **CRET** (torsion angle C−C−O−Me is 72°, see Table 3 and Figure 3).[31]

5. Aromatic Ring Expansion versus Degree of Charge Transfer upon $Cr(CO)_3$ Complexation. Structural changes as measured by the increase Δ in the average aromatic bond length of the cation radical **OMB**$^{\bullet+}$ relative to the neutral aromatic donor **OMB** are plotted in Figure 4 as a function of the number of electrons removed. Note that an intermediate point at 0.5 is also available from our previous structural study of the *dimeric* cation radical (**OMB)$_2$**$^{\bullet+}$, in which an electron is removed from a pair of equivalent cofacial donors.[14,32] The line in Figure 4 is arbitrarily drawn between **OMB** and **OMB**$^{\bullet+}$ to emphasize the linear relationship between bond-length changes of **OMB** and the (formal) number of electrons removed (i.e., oxidation).

The linear plot of the average bond-length changes in **OMB** in Figure 4 can be employed for a quantitative measure of the degree of electron redistribution upon complexation by Cr(CO)$_3$.[19]Thus the inclusion of the point for (**OMB**)Cr(CO)$_3$ onto the line in Figure 4 indicates that roughly one electron is redistributed from the **OMB** ligand onto the Cr(CO)$_3$ moiety. In other words, the degree of charge transfer from **OMB** upon Cr(CO)$_3$ complexation is roughly one.[34] Although the point for the NO$^+$ complex of **OMB** cannot be included,[35] we deem from the trend in Δ values listed in Table 4 that NO$^+$ complexation also results in about the same amount of electron redistribution.

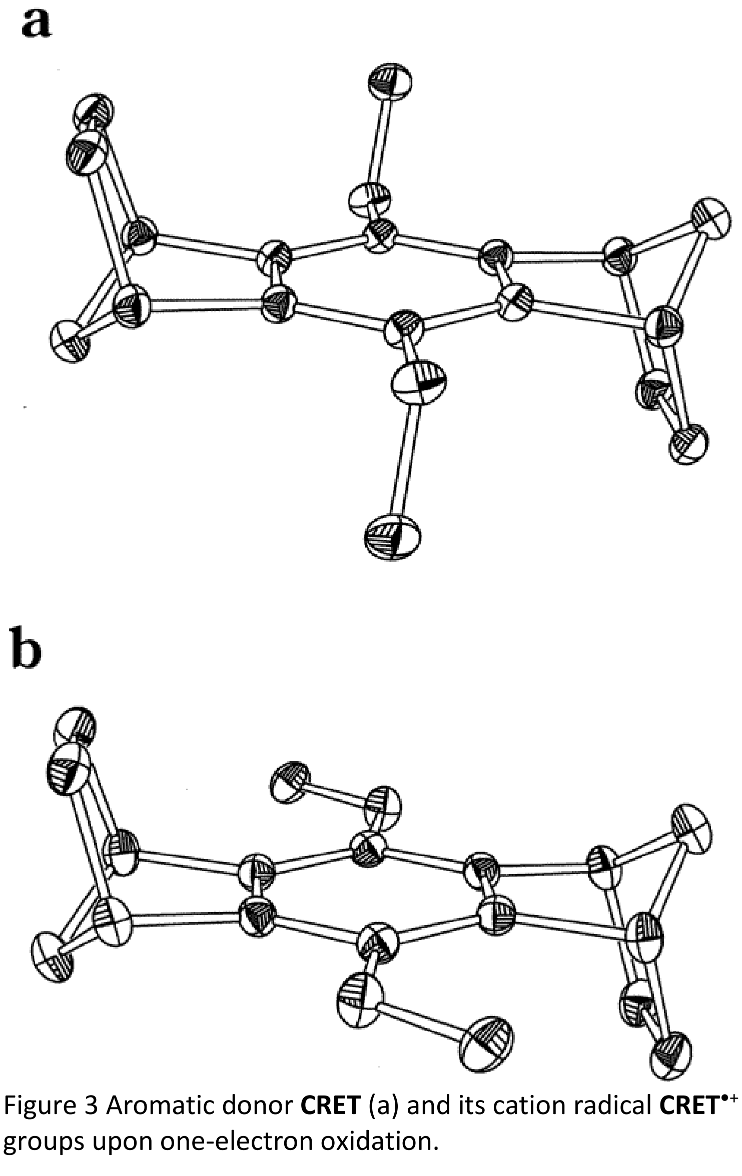


Figure 3 Aromatic donor **CRET** (a) and its cation radical **CRET**$^{\bullet+}$ (b) showing the 90° rotation of both methoxy groups upon one-electron oxidation.

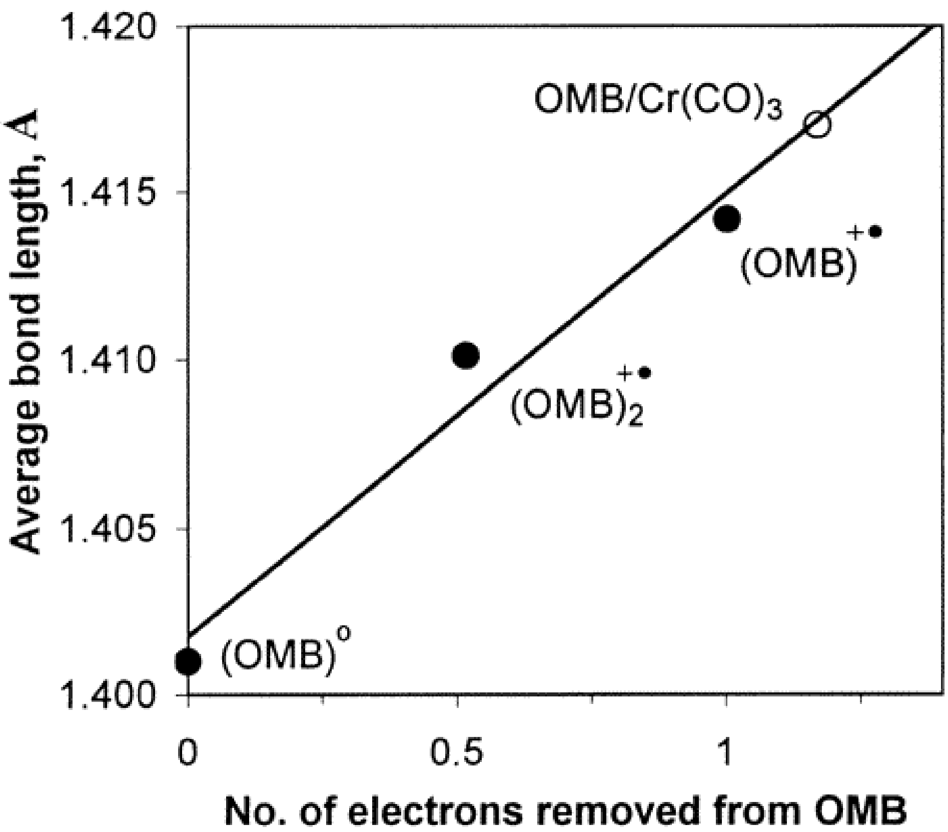


Figure 4 Linear increase in the average (aromatic) bond lengths in **OMB** attendant upon the successive removal of 0.5 and 1.0 electron in $(\mathbf{OMB})_2^{\bullet+}$ and $\mathbf{OMB}^{\bullet+}$, respectively. The fit of the point for the (**OMB**)$Cr(CO)_3$ complex indicates an effective degree of charge (electron) transfer of essentially unity.

Table 4. Comparative Expansion of Aromatic Donors in Ligand Complexation [$Cr(CO)_3$and NO^+] Relative to One-Electron Oxidation

	average ring expansion[a]		
arene	$\Delta_{D\bullet+}$	$\Delta_{Cr(CO)3}$	Δ_{NO+}
OMB	0.9(4)	1.0(3) [0.0/2.1]	
OMN	0.2(2)	0.7(3) [0.2/1.4]	0.4(5) [0.0/0.9]
CRET	1.1(2)	1.8(3)	1.3(4)

[a] The Δ values in pm are the average bond length in the complexed ligand (or cation radical) minus that in the neutral donor. The individual Δ values of the noncomplexed and complexed rings are given in brackets.

To quantify the degree of charge transfer in the $Cr(CO)_3$ complex of **CRET**, we compared the structural changes relative to the characteristic changes in the cation radical $\mathbf{CRET}^{\bullet+}$. We found that the average C−C bond length in the central aromatic ring increases by similar values in both **CRET** species, i.e., 1.8 pm in the chromium complex and 1.1 pm in the cation radical, indicating that the charge removed from **CRET** and transferred to the tricarbonylchromium cluster corresponds to about one electron. The degree of charge transfer from **CRET** can also be gauged by considering the orientation of the peripheral methoxy groups relative to the plane defined by the central aromatic ring (approximately perpendicular in neutral **CRET** and periplanar in the $\mathbf{CRET}^{\bullet+}$cation radical). Upon coordination with

Cr(CO)$_3$, both methoxy arms also rotate toward the aromatic plane (torsion angles C−C−O−Me are 46.5° and −30.5° for two symmetrically nonequivalent methoxy groups; see Figure 5a).[36]

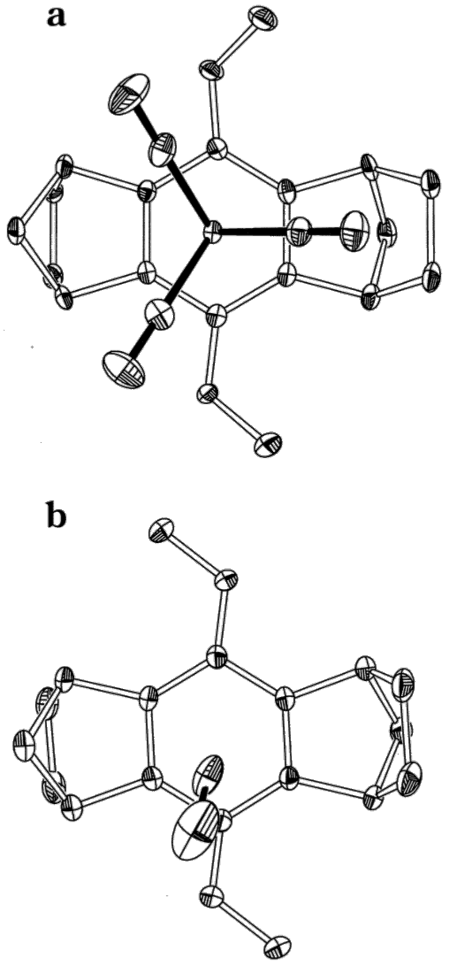


Figure 5 Rotation of the pair of methoxy groups in **CRET** (top perspective) upon its complexation with Cr(CO)$_3$ (a) and NO$^+$ (b). Compare with the conformational change of the methoxy groups in **CRET**$^{\bullet+}$ relative to **CRET** in Figure 3.

6. Comments on the Mechanism of Electron Redistribution in Arene Ligands upon Cr(CO)$_3$Complexation. A. Unsymmetrical Distortion in Polycyclic Aromatic Donors upon Complexation by Cr(CO)$_3$ and NO$^+$ Donors. The polycyclic aromatic donors **OMB** and **OMN** in class II provide some interesting insight into the mechanism of electron redistribution in the aromatic ligand upon complexation with Cr(CO)$_3$.

The X-ray crystal structure determination of (**OMB**)Cr(CO)$_3$ in Figure 6 reveals the average C−C bond length in the complexed ring to be dramatically increased by 2.1 pm, whereas that in the free ring remains unchanged within experimental error (see Table 4). Interestingly, the 2.1 pm elongation is twice that observed in both rings of the monomeric **OMB**$^{\bullet+}$ cation radical and therefore may be seen as the structural consequence of the transfer of approximately one electron with the positive charge concentrated in only one ring rather than delocalized over both rings of **OMB**.

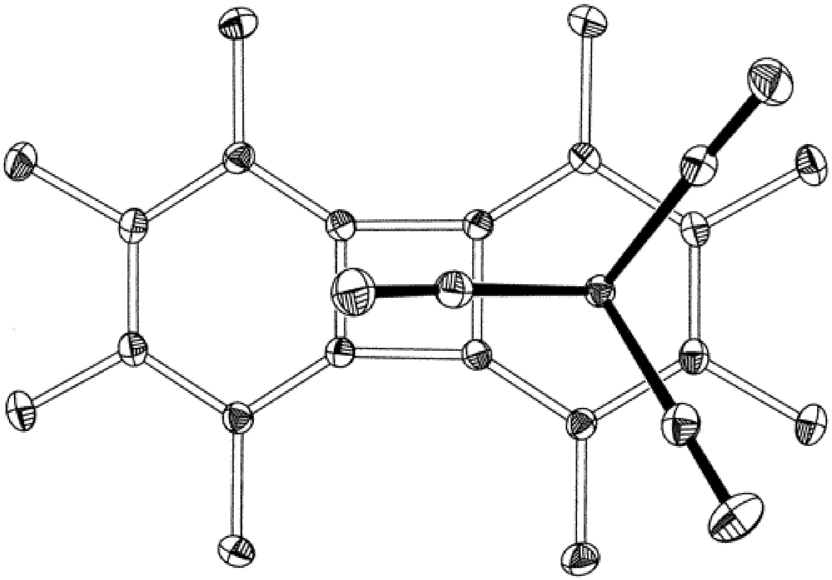


Figure 6 Complexation of $Cr(CO)_3$ with the biphenylene donor **OMB** showing preferential complexation with a single (benzenoid) ring only in a class II donor.

Similarly, in the naphthalenoid complex (**OMN**)$Cr(CO)_3$, the complexed ring (see Figure 7a) directly connected to the free ring experiences significant dilation, the average C−C bond length in the coordinated ring being 1.4 pm longer than that in neutral **OMN**, whereas the uncomplexed ring is largely unaltered. Both sets of structural data suggest that the electronic charge deficiency created in condensed aromatic hydrocarbons by the 1:1 complexation with $Cr(CO)_3$ remains localized on the complexed ring and that no significant electronic delocalization takes place between the connected rings to stabilize this deficiency.

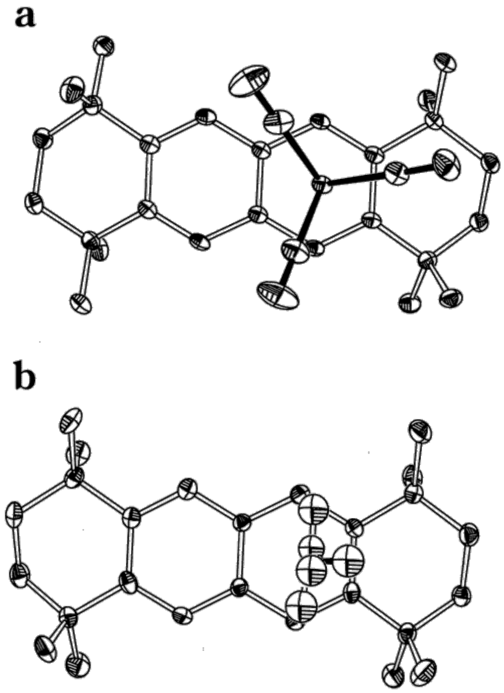


Figure 7 Complexation of the naphthalenoid donor **OMN** with $Cr(CO)_3$ (a) and NO^+ (b) showing the preferential complexation with a single (benzenoid) ring reminiscent of that shown for the biphenylene donor in Figure 6.

Whatever the mechanism of such an electron redistribution by $Cr(CO)_3$ may be, essentially the *same* applies to the main group acceptor NO^+. Figure 7b shows that the NO^+ acceptor in the 1:1 complex with **OMN** is located directly over only one of the six-membered aromatic rings.[37] As a result, the naphthalenoid chromophore in the NO^+ complex is subject to an unsymmetrical distortion: the average C−C bond length in the complexed ring increases by 0.9 pm, whereas the uncomplexed ring is essentially unaltered from that in the neutral donor **OMN** (Table 4).

In other words, the substantial delocalization of the charge deficiency created in a polyaromatic ligand upon coordination by the transition-metal acceptor $Cr(CO)_3$ is undistinguishable from that induced by NO^+ as the main group analogue in which d-orbital participation is not a relevant factor in the intermolecular bonding.

B. Bond Alternation in Benzenoid Donors upon Complexation by $Cr(CO)_3$ and NO^+. The comparable manner in which both $Cr(CO)_3$ and NO^+ distort aromatic ligands is also shown with class I donors, but in a more subtle way. For example, the X-ray crystallographic analysis of the hexamethylbenzene complex (**HMB**)$Cr(CO)_3$ at −150 °C reveals a significant (aromatic) bond alternation first observed in the benzene complex at −195 °C.[38] Thus, the three aromatic bonds eclipsed by the Cr−CO bond (see Figure 1a) are dramatically elongated by 2.5 pm, but the three staggered ones are essentially unaltered, being only slightly elongated by 0.5 pm. This result confirms the earlier theoretical analysis[39] and shows that the tricarbonylchromium cluster interrupts the conjugation in planar aromatic systems by inducing a significant short−long bond alternation within the complexed arene ligand.

Such a distortion induced by $Cr(CO)_3$ is strikingly reminiscent of that in the 1:1 complex of **HMB**with NO^+, the X-ray crystallographic structure of which is shown in Figure 2. In this charge-transfer complex, the NO^+ acceptor binds to the aromatic ring through the nitrogen center, which is at a short distance of 2.07 Å from the mean plane of the aromatic ring, and the N−O tilt eclipses one aromatic C−C bond, as shown in the top perspective (Figure 2b). Most notably, only that unique aromatic C−C bond which is eclipsed by $N{-}O^+$ is significantly elongated to 1.6 pm, whereas the remaining five bonds are unchanged within experimental error.[40,41]

In a similar vein, let us consider the class I aromatic donor **DMA** with both $Cr(CO)_3$ and NO^+ since the NO^+ complex shows a specific orientation of the acceptor.[41,42] For example, the neutral donor **DMA** possesses two kinds of C−C bonds in the central aromatic ring, i.e., two short α and four long β bonds, the difference being ca. 2 pm (Table 5). Upon complexation with $Cr(CO)_3$ (Figure 8A), one α and two β bonds are covered by CO arms. Again these covered (eclipsed) C−C bonds suffer from a greater elongation than the staggered ones, especially the two eclipsed β bonds that are elongated by 2.3 pm as compared with the two staggered ones. The same phenomenon is observed in the **DMA** complex with the nitrosonium acceptor, in which NO^+ is displaced from the center of the aromatic ring and tilted toward one β C−C bond (Figure 8b). It is specifically this bond that becomes 1.1 pm longer, whereas the three other β bonds are unchanged within experimental error (0.2 pm). This result is consistent with that obtained with [**HMB**, NO^+] and shows that the noncovalent complexation with NO^+ leads to a repulsion of electron density of the eclipsed C−C bond without significantly affecting the other bonds.

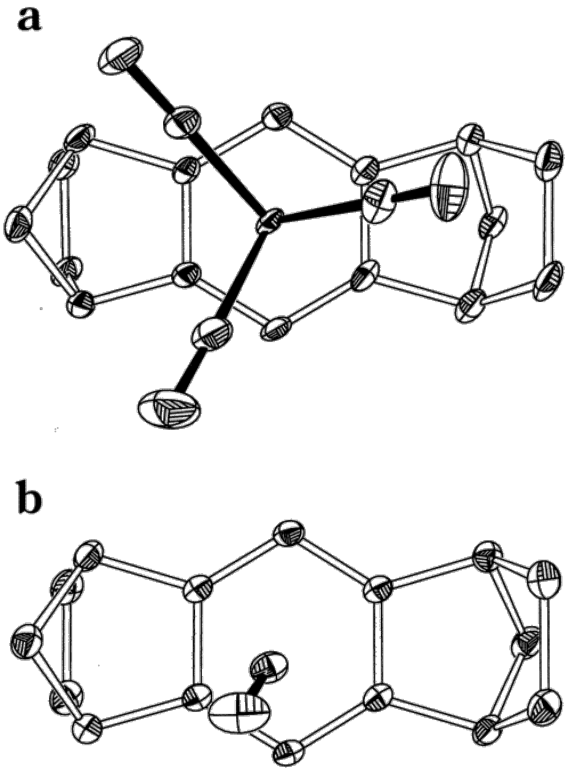


Figure 8 Complexation of the sterically hindered benzenoid donor **DMA** with $Cr(CO)_3$ (a) and NO^+ (b), showing the strong similarity in their bonding (*exo* and *endo*) modes.

Let us now consider the sterically encumbered donor **CRET**, in which we earlier described (structure **D**) the quinoidal distortion similar to that observed upon one-electron oxidation. A closer inspection shows the distortion of the aromatic ring of **CRET** by $Cr(CO)_3$ akin to that in **DMA**. In particular, the α bond which is eclipsed by a Cr−CO bond in Figure 5a is elongated by 3.1 pm more than the staggered α bond, and the two eclipsed β bonds are stretched by more than 1.6 pm relative to the two staggered ones. In a related manner, **CRET** also suffers the same kind of distortion upon complexation with $Cr(CO)_3$ and NO^+. With the NO^+ complex, two crystallographically independent units are observed that differ only in the location of the acceptor. In crystal unit **A**, the tilted NO^+ acceptor lies on the edge of the central ring of **CRET** and eclipses one β bond (Figure 5b) which is 0.8 pm longer than the average of the three other β bonds. In crystal unit **B**, the NO^+ is more vertical and lies closer to the centroid. As a result, there is no marked distinction between eclipsed/staggered β bonds, and all the β bonds are more or less equally elongated (by 1.4 pm).

The conformational dependence of the NO^+ acceptor on the aromatic distortion of **CRET** as described above is also underscored in the structure of the [**HEB**, NO^+] complex, in which NO^+ is sterically constrained to lie (vertically) along the centroid axis (Figure 9). As a result, there can be only one type of aromatic C−C bond, and it is important to note that all aromatic bonds are equally elongated by 1.4 pm. Such a homogeneous elongation of all aromatic bonds is not an intrinsic property of **HEB**, since the characteristic bond alternation like that in (**HMB**)Cr(CO)$_3$ (vide supra) is observed upon Cr(CO)$_3$ complexation.

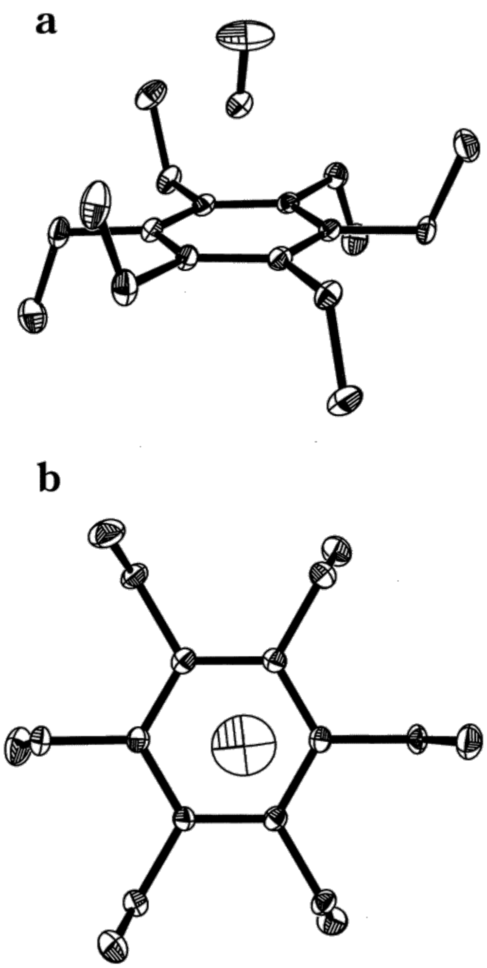


Figure 9 Axial bonding of NO$^+$ along the 3-fold symmetry axis of the sterically encumbered **HEB** donor in side (45°) and top perspectives (a and b, respectively), showing the equivalence of all aromatic C−C bonds in contrast to those in the [**HMB**, NO$^+$] complex in Figure 2.

Steric encumbrance can also act in another way on the aromatic donor to orient the tripodal Cr(CO)$_3$ in such a way that the carbonyl “arms” will eclipse the shorter C−C aromatic bonds and thus compete for electron density in the free ligand. For example, the hindered aromatic donor **TET** possesses an alternating sequence of long α bond and shorter β bonds arising from the Mills−Nixon effect.[43] In (**TET**)Cr(CO)$_3$, steric hindrance by the bicyclohexyl substituents forces the Cr(CO)$_3$ to orient its CO arms over the short β bonds, as shown in Figure 1b. In turn, both eclipsed (α) and staggered (β) bonds of the aromatic ring are lengthened upon complexation, but the eclipsed ones are much more altered (+3.0 pm instead of +0.8 pm for the staggered ones). Consequently, the previously short β bonds in the free ligand are elongated by 0.5 pm more than the α bonds in the chromium complex because of the effect of the carbonyl groups. Thus the (η^6-**TET**)Cr(CO)$_3$ complex may be seen as a complex in which structural constraints due to the Mills−Nixon effect and those originating from the coordination of Cr(CO)$_3$ oppose each other and lead to an almost complete cancellation of bond-length alternation in **TET**. As a result, an interesting comparison can be made between the chromium complexes of **HMB** and **TET**. The effect of $Cr(CO)_3$ on these ligands remains the same upon complexation (expansion of the eclipsed C−C bonds), but it leads to opposite results, that is, the interruption of conjugation in (η^6-**HMB**)$Cr(CO)_3$ but almost complete equalization of all C−C bonds in (η^6-**TET**)$Cr(CO)_3$. As a comparison, it is to be noted that in the nitrosonium complex [**TET**, NO^+], the central ring gets larger, but the β bonds on one hand and the α bonds on the other hand expand homogeneously.

Summary and Conclusions

Arenes such as benzene (Ar) are electron donors by virtue of their ready (i) one-electron oxidation to cation radicals ($Ar^{\bullet+}$),[12] (ii) formation of charge-transfer complexes [Ar,A] with π-acceptors such as A = nitrosonium cation (NO^+),[20] (iii) self-association to form dimeric cation radicals ($Ar_2^{\bullet+}$),[33]and (iv) complexation with coordinatively unsaturated transition-metal fragments such as ML_n = $Cr(CO)_3$ to form the π-coordination complexes (η^6-Ar)$Cr(CO)_3$,[4] as schematically represented in Chart 2.

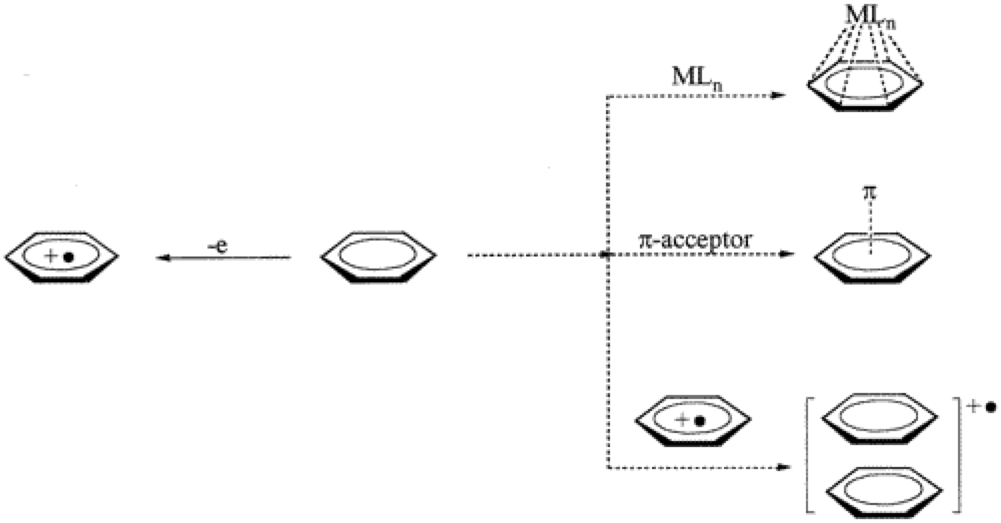


Chart 2

In this report, we show that the precise measurement of the structural changes in the arene ligand provides considerable insight into the common nature of such intermolecular interactions.

Complexation of various arene donors with $Cr(CO)_3$ invariably lead to significant ring expansion. In fact, the magnitude of the structural change quantitatively parallels that observed in the production of the cation radical ($Ar^{\bullet+}$) itself and in the complexation with nitrosonium cation as the prototypical (main group) electron acceptor in charge-transfer complexes [Ar, NO^+] as classified by Mulliken.[23,24] As such, the transfer (outflow) effectively of a full unit of charge from the aromatic ligand is a common characteristic of the intermolecular interactions in Chart 2.

The detailed comparison of the structural changes in various aromatic ligands shows that complexation by $Cr(CO)_3$ and NO^+ effects the same type of ring distortion, leading on one hand to selective ring enlargement of polycyclic aromatic donors of class II and on the other hand to specific bond alternation in benzenoid donors in class I. We believe both types of distortion are intimately related to the donor/acceptor bonding and underscore the *common* nature of intermolecular bonding of an arene ligand, be it with a transition metal [$Cr(CO)_3$] or main group [NO^+] acceptor. As such, we hope that the collaborative interaction now in progress will provide the theoretical basis for unifying the classical concepts of *ligand coordination* with the Mulliken concept of *charge transfer.*

Experimental Section

Materials. Hexamethylbenzene (**HMB**) (Aldrich) and hexaethylbenzene (**HEB**) (Acros) were purified by repeated crystallization from ethanol and heptane. The synthesis of the various electron donors such as 9,10-dimethoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene (**CRET**),[31] 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene (**DMA**),[44]1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-1,4:5,8:9,12-trimethanotriphenylene (**TMT**),[45]1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-1,4:5,8:9,12-triethanotriphenylene (**TET**),[46]1,2,3,4,5,6,7,8-octamethylbiphenylene (**OMB**),[47] and 1,2,3,4,7,8,9,10-octahydro-1,1,4,4,7,7,10,10-octamethylnaphthacene (**OMN**)[48] have been described previously. $Cr(CO)_6$ was purchased from Acros Chemical Co. and used without any further purification. Nitrosonium hexachloroantimonate[49] was stored in a Vacuum Atmosphere HE-493 drybox kept free of oxygen. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (∼20 vol %) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexane, toluene, and tetrahydrofuran were distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (∼12 h). After distillation from CaH_2, the solvents were stored in the Schlenk flasks under an argon atmosphere. The dibutyl ether was purchased from Aldrich Chemical Co. and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings.

The cation radicals of octamethylbiphenylene (**OMB**) and of the hydroquinone ether **CRET** were prepared by using triethyloxonium hexachloroantimonate as oxidant.[14]

Preparation of (η^6-Arene)Tricarbonylchromium Complexes. The tricarbonylchromium complexes of hexamethylbenzene (**HMB**), the hydroquinone ether **CRET**, dimethanoanthracene (**DMA**), triethanotriphenylene (**TET**), octamethylbiphenylene (**OMB**), and octamethylnaphthacene (**OMN**) have been prepared according to the method of Mahaffy and Pauson,[15] as follows.

General Procedure. Typically, in a 50 mL flask fitted with a Schlenk adapter and under argon flow were placed hexacarbonylchromium (100 mg, 0.45 mmol), the neutral arene (1 equiv), dibutyl ether (20 mL), and tetrahydrofuran (2 mL). The argon stream was stopped, and the mixture was heated at reflux for 24 h. Upon slow cooling, well-shaped yellow crystals of (η^6-arene)tricarbonylchromium suitable for X-ray single-crystal analysis separated from the solution.

X-ray Crystallography. The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using Mo Kα radiation (λ = 0.71073 Å), at −150 °C unless otherwise specified. The structures were solved by direct methods[50] and refined by fullmatrix least-squares procedure with IBM Pentium and SGI O_2 computers. [Note that the X-ray structure details of various compounds mentioned here are on deposit and can be obtained from Cambridge Crystallographic Data Center, U.K.]

Crystal Data for HMB.[51] Brutto formula: $C_{12}H_{18}$. MW = 162.26, triclinic $P\bar{1}$, a = 5.2602(2), b = 6.1990(3), c = 8.0040(3) Å, α = 103.818(1)°, β = 98.718(1)°, γ = 100.192(1)°, D_c = 1.103 g cm^{-3}, V= 244.26(3) Å^3, Z = 1. The total number of reflections measured was 2363, of which 1622 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0469 and w$R2$ = 0.1330 for 1403 reflections with $I > 2\sigma(I)$.

Crystal Data for DMA. Brutto formula: $C_{16}H_{18}$. MW = 210.30, monoclinic $C2/c$, a = 10.5037(6), b= 5.5865(3), c = 19.400(1) Å, β = 92.563(1)°, D_c = 1.228 g cm^{-3}, V = 1137.2(1) Å^3, Z = 4. The total number of reflections measured was 7207, of which 2594 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0973 and w$R2$ = 0.2285 for 1773 reflections with $I > 2\sigma(I)$.

Crystal Data for TET.[52] Brutto formula: $C_{24}H_{30}$. MW = 318.48, monoclinic $P2_1/c$, a = 15.5421(4), b = 10.2264(3), c = 11.4845(3) Å, β = 100.692(1)°, D_c = 1.179 g cm^{-3}, V = 1793.65(8) Å^3, Z = 4. The total number of reflections measured was 22 484, of which 8114 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0550 and w$R2$ = 0.1202 for 8110 reflections with $I > 2\sigma(I)$.

Crystal Data for OMB.[53] Brutto formula: $C_{20}H_{24}$. MW = 264.39, monoclinic $C2/m$, at −180 °C, a = 11.459(2), b = 7.003(1), c = 9.985(2) Å, β = 106.67(3)°, D_c = 1.144 g cm^{-3}, V = 767.6(8) Å^3, Z = 2. The total number of reflections measured was 4090, of which 1748 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0628 and w$R2$ = 0.1256 for 377 reflections with $I > 2\sigma(I)$.

Crystal Data for OMN. Brutto formula: $C_{26}H_{36}$. MW = 348.55, monoclinic $P2_1/n$, a = 5.8991(1), b= 22.0559(5), c = 8.3897(2) Å, β = 108.880(1)°, D_c = 1.121 g cm^{-3}, V = 1032.85(4) Å^3, Z = 2. The total number of reflections measured was 12 915, of which 4646 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0478 and w$R2$ = 0.1232 for 3926 reflections with $I > 2\sigma(I)$.

Crystal Data for CRET.[54] Brutto formula: $C_{18}H_{22}O_2$. MW = 270.36, triclinic $P\bar{1}$, a = 5.8113(1), b = 8.5913(2), c = 14.4752(1) Å, α = 85.457(1)°, β = 89.104(1)°, γ = 77.373(1)°, V = 703.00(2) Å^3, Z = 2. The total number of reflections measured was 8917, of which 6122 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0474 and w$R2$ = 0.1114 for 5061 reflections with $I > 2\sigma(I)$.

Crystal Data for CRET Cation Radical.[55] Brutto formula: $C_{18}H_{22}Cl_6O_2Sb$. MW = 604.81, monoclinic $P2_1/c$, a = 8.4582(3), b = 14.3770(5), and c = 9.9283(3) Å, β = 112.334(1)°, V = 1116.75(6) Å^3, Z = 2. The total number of reflections measured was 14 307, of which 5005 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0200 and w$R2$ = 0.0421 for 3894 reflections with $I > 2\sigma(I)$.

Crystal Data for (η^6-HMB)Cr(CO)$_3$ Complex.[56] Brutto formula: $C_{15}H_{18}CrO_3$. MW = 298.29, orthorhombic $Pbca$, at −180 °C a = 13.5997(5), b = 13.2814(5), c = 15.1233(6) Å, D_c = 1.451 g cm^{-3}, V = 2731.6(1) Å^3, Z = 8. The total number of reflections measured were 38 002, of which 5978 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0254 and w*R*2 = 0.0722 for 5045 reflections with *I* > 2σ(*I*).

Crystal Data for (η^6-DMA)Cr(CO)$_3$ Complex. Brutto formula: $C_{19}H_{18}CrO_3$. MW = 346.33, monoclinic *P*2$_1$/*c*, *a* = 9.8790(3), *b* = 12.7753(4), *c* = 12.5201(4) Å, β = 104.85(1)°, *D*$_c$ = 1.506 g cm^{-3}, *V* = 1527.3(1) Å^3, *Z* = 4. The total number of reflections measured were 18 781, of which 6717 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0759 and w*R*2 = 0.1589 for 3904 reflections with *I* > 2σ(*I*).

Crystal Data for (η^6-TET)Cr(CO)$_3$ Complex. Brutto formula: $C_{27}H_{30}CrO_3$. MW = 454.51, orthorhombic *Pnma*, *a* = 13.6584(3), *b* = 15.5046(3), *c* = 10.0386(3) Å, *D*$_c$ = 1.420 g cm^{-3}, *V* = 2125.9(1) Å^3, *Z* = 4. The total number of reflections measured were 26 708, of which 5103 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0481 and w*R*2 = 0.0882 for 3505 reflections with *I* > 2σ(*I*).

Crystal Data for (η^6-OMB)Cr(CO)$_3$ Complex. Brutto formula: $C_{23}H_{24}CrO_3$. MW = 400.42, monoclinic *P*2$_1$/*c*, at −180 °C, *a* = 9.2859(5), *b* = 12.5942(7), *c* = 16.1218(9) Å, β = 94.313(1)°, *D*$_c$= 1.415 g cm^{-3}, *V* = 1880.1(2) Å^3, *Z* = 4. The total number of reflections measured were 23 647, of which 8322 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0397 and w*R*2 = 0.0903 for 6467 reflections with *I* > 2σ(*I*).

Crystal Data for (η^6-OMN)Cr(CO)$_3$ Complex. Brutto formula: $C_{29}H_{36}CrO_3$. MW = 484.58, monoclinic *P*2$_1$/*n*, *a* = 12.6747(2), *b* = 15.2089(2), *c* = 13.0697(2) Å, β = 90.544(1)°, *D*$_c$ = 1.278 g cm^{-3}, *V* = 2519.3(1) Å^3, *Z* = 4. The total number of reflections measured were 32 012, of which 11 493 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0625 and w*R*2 = 0.1160 for 6131 reflections with *I* > 2σ(*I*).

Crystal Data for (η^6-CRET)Cr(CO)$_3$ Complex. Brutto formula: $C_{21}H_{22}CrO_5$. MW = 406.39, monoclinic *P*2$_1$/*n*, *a* = 10.9954(5), *b* = 11.4633(5), *c* = 14.4954(12) Å, β = 91.072(1)°, *D*$_c$ = 1.478 g cm^{-3}, *V* = 1826.7(2) Å^3, *Z* = 4. The total number of reflections measured were 23 054, of which 8277 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0598 and w*R*2 = 0.0976 for 4588 reflections with *I* > 2σ (*I*).

Crystal Data for [HMB, NO$^+$SbF$_6^-$] Complex. Brutto formula: $C_{12}H_{18}F_6NOSb$. MW = 428.02, monoclinic *C*2/*c*, *a* = 12.9243(3), *b* = 17.9474(4), *c* = 13.3904(4) Å, β = 100.090(1)°, *D*$_c$ = 1.859 g cm^{-3}, *V* = 3058.0(1) Å^3, *Z* = 8. The total number of reflections measured were 18 967, of which 6941 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0291 and w*R*2 = 0.0608 for 5652 reflections with *I* > 2σ(*I*).

Crystal Data for [DMA, NO$^+$SbCl$_6^-$] Complex. Brutto formula: $C_{16}H_{18}Cl_6NOSb$. MW = 574.76, monoclinic *P*2$_1$/*c*, *a* = 8.0724(2), *b* = 17.2516(4), *c* = 15.0853(3) Å, β = 91.680(1)°, *D*$_c$ = 1.818 g cm^{-3}, *V* = 2099.9(1) Å^3, *Z* = 4. The total number of reflections measured were 25 586, of which 9514 reflections were symmetrically nonequivalent. Final residuals were *R*1 = 0.0238 and w*R*2 = 0.0494 for 8457 reflections with *I* > 2σ(*I*).

Crystal Data for [TMT, $NO^+SbCl_6^-$]·1/2CH_2Cl_2·1/4C_7H_8 Complex. Brutto formula: $C_{23.25}H_{27}Cl_6NOSb$. MW = 706.36, triclinic $P\bar{1}$, a = 10.3371(1), b = 13.5511(2), c = 20.7179(3) Å, α = 92.498(1)°, β = 99.831(1)°, γ = 102.093(1)°, D_c = 1.684 g cm^{-3}, V = 2786.6(1) $Å^3$, Z = 4. The total number of reflections measured were 45 575, of which 24 220 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0610 and w$R2$ = 0.1021 for 16 607 reflections with $I > 2\sigma(I)$.

Crystal Data for [OMN, $NO^+SbCl_6^-$]·2CH_2Cl_2 Complex. Brutto formula: $C_{28}H_{40}Cl_{10}NOSb$. MW = 882.86, orthorhombic $P2_12_12_1$, a = 12.7689(3), b = 13.0980(3), c = 22.4779(1) Å, D_c = 1.560 g cm^{-3}, V = 3759.4(1) $Å^3$, Z = 4. The total number of reflections measured were 44 079, of which 16 677 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0614 and w$R2$ = 0.1127 for 12 559 reflections with $I > 2\sigma(I)$.

Crystal Data for [CRET, $NO^+SbCl_6^-$] Complex. Brutto formula: $C_{18}H_{22}Cl_6NO_3Sb$. MW = 634.82, monoclinic $P2_1$, a = 8.8385(1), b = 20.9771(2), c = 12.7867(1) Å, β = 91.567(1)°, D_c = 1.779 g cm^{-3}, V = 2369.85(4) $Å^3$, Z = 4. The total number of reflections measured were 43 584, of which 20 632 reflections were symmetrically nonequivalent. Final residuals were $R1$ = 0.0353 and w$R2$ = 0.0739 for 18 131 reflections with $I > 2\sigma(I)$.

Acknowledgment

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Supporting Information Available

Tables 5−94 containing X-ray crystal data, atomic coordinates and thermal displacement parameters, and bond lengths and angles for 18 compounds/complexes studied (see Experimental Section). This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added in Proof: The X-ray structure of **TET**$^{\bullet+}SbCl_6^-$ has been recently reported, but the low precision does not allow any reasonable structural analysis. See: Matsuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007.

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[19] Hereinafter we adopt the average bond distance (*d*) as the *linear* approximation for the ring enlargement owing to our primary concern about the relative change of the arene upon its complexation. For $\Delta < 10$ pm, the error in this linear approximation is <10% (see Figure 4). Thus ring expansion of an aromatic ligand upon $Cr(CO)_3$ or NO^+ complexation is a result of decrease in the π-electron density according to eq 1.

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[36] Interestingly, both methoxy groups deviate from the plane of the benzene ring *toward* the coordinated $Cr(CO)_3$ fragment, heedless of steric hindrance. This conformation can be attributed to an *agostic*(attractive) interaction between the activated methyl group (that bears a partial positive change, see structure **C** and δ values in Table 3 for **CRET**) and the chromium center. Remarkably, the observed CH···Cr distances (3.36 and 3.50 Å) are shorter than those calculated from idealized positions (along the C−O bond) of hydrogens (3.43 and 3.56 Å, respectively). This structure confirms the observed conformational changes not to be a consequence of steric hindrance created by $Cr(CO)_3$, but the result of charge removal from**CRET**.

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