

Structural Effects of Group VI Metal Tricarbonyl Binding to Benzenoid Rings: Interruption of Conjugation or Enhanced Aromaticity?

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Dedicated to *Jack D. Dunitz* on the occasion of his 80th birthday. His analytical mind and eternal energy are a constant source of inspiration.

The effect of tricarbonyl (group VI metal) complexation on the geometric aromatic character of benzenoid rings is studied as a function of bond-length alternation (localization) in the parent arene. Good agreement between theory and experiment is established for (η^6 -benzene) tricarbonylchromium, -molybdenum, and -tungsten. It is found that, whereas the electrons of benzene become slightly more localized upon tricarbonyl metal complexation, those of 'cyclohexatriene' mimics, like *in*-starphenylene, become more delocalized. A combination of *ab initio* quantum-mechanical and high-accuracy X-ray methods leads to a linear structure–structure correlation between the free and metal-bound arene bond-alternation geometry. In all cases, the average bond length in the arene increases upon complexation. The computational observation that the average bond length increases more in benzene complexes than in *in*-starphenylene implies stronger back bonding in the benzene complexes and coincides with the experimental observation that more-delocalized arenes form thermodynamically favored complexes. The rotational barriers about the tricarbonylmetal-to-arene axis were computed for **1-Cr**, **1-Mo**, and **1-W** as well as for **5-Cr**, **5-Mo**, and **5-W**. Barriers for the former group are characteristically low, almost negligible (0.05 kcal/mol for **1-Cr**; 0.01 kcal/mol for **1-Mo**; 0.27 kcal/mol for **1-W**), whereas for the latter group they are substantial (11.2 kcal/mol for **5-Cr**; 15.2 kcal/mol for **5-Mo**; 13.6 kcal/mol for **5-W**). The higher barriers found in **5-M** compounds are consistent with previous findings.

1. Introduction. – The benzene ring of (η^6 -benzene)tricarbonylchromium (**1-Cr**) displays two characteristic bond-length distortions compared to benzene (**1**): the overall average bond length Q (*vide infra*) increases, and the bond lengths alternate (long/short) around the ring in a three-fold symmetric manner.¹⁾ The group-VI cognates with molybdenum (see **1-Mo**) and tungsten (see **1-W**) follow the same pattern but the distortions are of slightly larger magnitude²⁾. The increase in the overall average bond length can be viewed as coming from removal of electron density by the metal from the bonding HOMO/HOMO' on benzene and/or back-donation of electron density by the metal to the antibonding LUMO/LUMO' on benzene [2]. The three-fold symmetrical distortion reflects the three-fold symmetric nature of the tricarbonyl chromium tripod. Oddly, the bond lengths described in these studies betray a greater

1) For a low-temperature high-accuracy X-ray structure of (benzene)tricarbonylchromium, see [1a,b].

2) For a low-temperature high-accuracy X-ray structure of (benzene)tricarbonylmolybdenum, see [1c]; for an X-ray structure of (benzene)tricarbonyltungsten, see [1d].

elongation of the bonds located in classically trigonal prismatic positions (*cis* to the carbonyls) than those in the classically octahedral positions (*trans* to the carbonyls; see Fig. 1). A classical molecular-orbital picture for (η^6 -cyclohexatriene)tricarbonylchromium (**2-Cr**) would predict that the octahedral (*trans*) positions should elongate more [3]. This difference in structural response to complexation between what is observed for **1-Cr**, and what is predicted for **2-Cr** motivated us to search for a structure correlation across a series of arenes and their (arene)tricarbonylchromium complexes, wherein the π bonds in the arene are already partially localized to variable extents³⁾. The results of such an analysis suggests that tricarbonylmetal complexation can lead to greater or lesser bond-length alternation ('geometric aromaticity') in an arene depending on the initial localized nature of the ring.

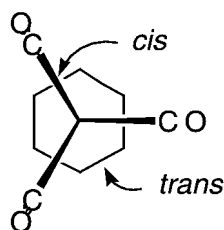
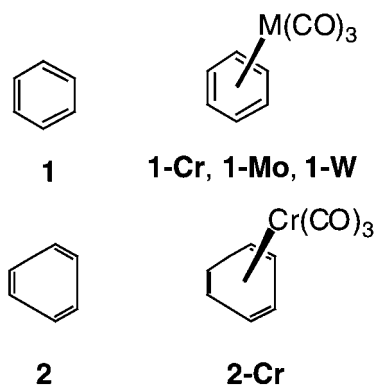


Fig. 1. Projection down the metal-tripod-to-arene axis

2. Computational Methods. – All calculations have been carried out with the Gaussian98 [5] and GAMESS [6] software packages, running on the hardware facilities at the *San Diego Supercomputer Center*. The molecular structures and associated energetics were determined by means of a variety of levels of theory to establish self-consistency in terms of basis sets as well as effects of dynamic correlation. Hybrid density functional theory (HDFT) methods were employed, by using *Becke's* 3-parameter hybrid exchange functional [7] in combination with the nonlocal correlation functional provided by the *Lee–Yang–Parr* expression [8], B3LYP. The 6-311G(2d,p)

³⁾ This simple observation was reported earlier [4].

and 6-311 G(d,p) triple- ζ and 6-31G(d,p) double- ζ basis sets were compared and analyzed in combination with the appropriate transition metal basis sets [9][10]. These levels of theory have been previously shown to be reliable for these types of compounds [11][12]. *Hay* and *Wadt* relativistic effective core potentials (RECP) [13] were used for the transition metals, Mo and W. The specific effective core potential/basis set combination used was LANL2DZ (Los Alamos National Laboratory 2-double- ζ ; the '2' indicating that the valence and 'valence-1' shells are treated explicitly) [14]. The LANL2DZ basis set is of double- ξ quality in the valence and 'valence-1' shells, while the RECP contains *Darwin* and mass-velocity contributions [14–16]. Because the Cr compounds can be computed fully with 6-311G(2d,p), for comparative purposes, all Cr compounds were computed with the same core potentials as for Mo and W. We noticed no significant differences between predictions from triple- and double- ζ basis sets nor between (2d,p) and (d,p) polarization functions. Full geometry optimizations were performed, and subsequent Hessians (matrix of second derivatives) were calculated to determine local minima (positive definite) or an *n*th-order saddle point (*n* negative eigenvalues). From the fully optimized structures, single-point-energy computations were performed by the MP2 [17] dynamic-correlation treatment for additional comparisons against that provided by HDFT methods, particularly for the analysis of chemical and physical properties such as orbital analysis and barrier heights. Molecular-orbital contour plots, used as an aid in the discussion of the results, were generated with the program 3D-PLTORB [18], and depicted with QMView [19–21].

3. Results. – A series of arenes comprising benzene (**1**), biphenylene (**3**), angular terphenylene (= benzo[3,4]cyclobuta[1,2-*a*]biphenylene; **4**), and starphenylene (= bisbenzo[3,4]cyclobuta[1,2-*a*:1',2'-*c*]biphenylene; **5**) provides six benzenoid rings of varying degree of bond length alternation⁴). At the extremes of this series, benzene is six-fold symmetrical with no bond-length alternation ($a = b = 1.395 \text{ \AA}$), whereas the central ring of starphenylene (**5**) is three-fold symmetrical with bond-length alternation of 15 pm ($a_{endo} = 1.49 \text{ \AA}$; $b_{exo} = 1.34 \text{ \AA}$).

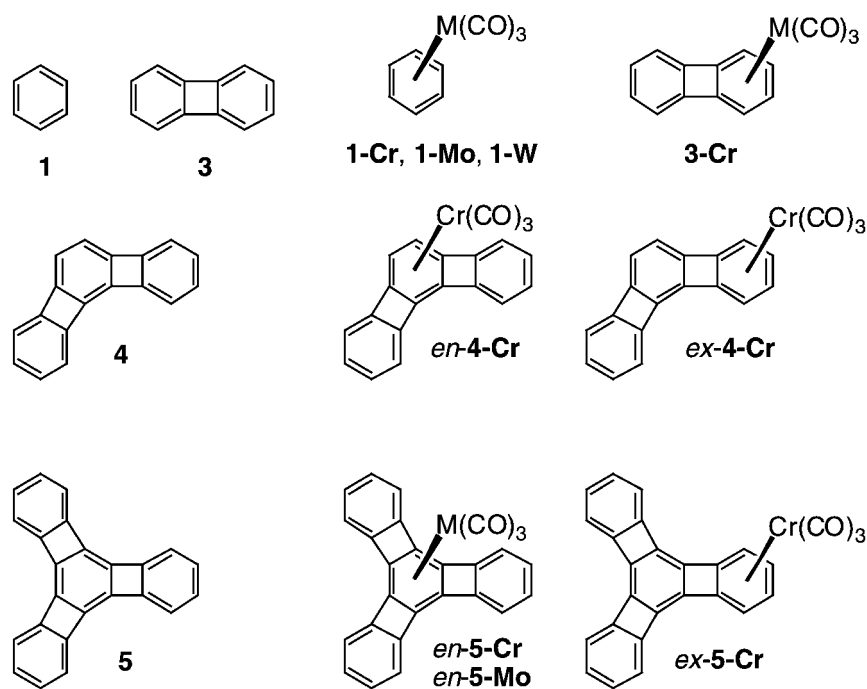
The bond-length changes that occur in each benzenoid ring upon complexation with a tricarbonyl (group VI metal) fragment were assessed by the increase in the average ring C–C bond (ΔQ value; *Eqn. 1*) as well as by the degree to which those bonds in trigonal-prismatic sites lengthened compared to those in octahedral sites ($\Delta\delta$ value; *Eqn. 2*). The former parameter provides a gauge of how much the total bond order in the ring changes, and the latter provides a gauge of the (de)localizing effect of complexation.

$$\Delta Q = Q_{\text{arene-metal}} - Q_{\text{arene}}; Q = \text{average C–C bond length} \quad (1)$$

$$\Delta\delta = \delta_{\text{arene-metal}} - \delta_{\text{arene}}; \delta = d_{cis} - d_{trans} \text{ or } d_{exo} - d_{endo}; d = \text{C–C bond length} \quad (2)$$

For benzene, the three group-VI cognates are known, and high-quality experimental data are available (*Table 1*). In all three complexes, the average bond length increases by *ca.* 2 pm, and the bond *cis* to the carbonyl elongates *ca.* 2 pm more than the ones

⁴) The results presented here come from *ab initio* quantum-mechanical (QM) computations.



trans to the carbonyl. These distortions are present in every case and consistent in the interpretation of both computation and experiment. In the putative rotational transition state, where the carbonyl ligands eclipse alternate benzene C-atoms rather than alternate C–C bonds, the computed ΔQ value is essentially identical to that of the rotational ground state. The rotational barrier is very low for all three metal complexes (<0.4 kcal/mol).

Table 1. *X-Ray and Ab Initio Structural Parameters for 1-Cr, 1-Mo, and 1-W*

Compound	Method	<i>cis</i> [Å]	<i>trans</i> [Å]	<i>Q</i> [Å]	ΔQ^a [pm]	$\Delta\delta$ [pm]	<i>Q</i> ⁺ [Å]	ΔQ^+ [pm]	Barrier [kcal/mol]
1-Cr	exper.	1.423	1.406	1.415	2.0	1.7			
	QM ^{b)}	1.419	1.399	1.409	1.8	2.0	1.400	0.9	0.03
	QM ^{c)}	1.411	1.388	1.400	0.9	2.3			0.4
	QM ^{d)}								(0.05)
1-Mo	exper.	1.423	1.403	1.413	1.8	2.0			
	QM ^{c)}	1.419	1.388	1.404	1.3	3.1	1.403	1.2	0.31
	QM ^{d)}								(0.01)
1-W	exper.	1.424	1.397	1.411	1.6	2.7			
	QM ^{c)}	1.421	1.395	1.408	1.7	2.6	1.408	1.7	0.15
	QM ^{d)}								(0.27)

^{a)}*Q* for benzene 1.395 (exper.); 1.391 (QM). ^{b)}B3LYP/6-311G(2d,p). ^{c)}RHF/6-311G(d,p). ^{d)}MP2/6-31G(d,p)//RHF/6-31G(d,p).

Biphenylene (**3**) has two symmetry-related benzenoid rings, which lead to only one tricarbonylmonochromium adduct **3-Cr**. In contrast, the benzenoid rings of **4** and **5**⁵) fall into two classes, a unique internal ring (ligand denoted by *in-4* and *in-5*) and a symmetry-related set of two or three external rings (ligand denoted by *ex-4* and *ex-5*, resp.). Thus, tricarbonylmetal complexation of **4** and **5** leads to four complexes: *in-4-Cr*, *ex-4-Cr*, *in-5-Cr*, and *ex-5-Cr*.

Tricarbonyl metal complexation shows a differing effect on the degree of bond-length alternation in these six cases (*Table 2*). For **1**, which is fully six-fold symmetric as a free arene, the average bond-length increases, as does the bond-length alternation upon formation of **1-Cr**. For **5**, which is only three-fold symmetric and has a high degree of bond-length alternation (cyclohexatriene-like), the average bond-length still increases, but the bond-length alternation decreases. Overall, the degree to which *Q* increases is rather constant ($\Delta Q = 1.8 \pm 0.2$ pm) with the exception of **5/5-Cr** (1.1 pm). This constant effect on *Q* suggests that the overall degree of metal–arene (back)-bonding is similar across the series until the localized extreme.

Table 2. Ab initio RHF/6-31G(d,p) Structural Parameters for **1**, **3–5**, and Their [Cr(CO)₃] Complexes

Compound	<i>cis (endo)</i> [Å]	<i>trans (exo)</i> [Å]	<i>Q</i> [Å]	ΔQ [pm]	δ [pm]	$\Delta\delta$ [pm]
1	1.391	1.391	1.391	–	0	–
1-Cr	1.419	1.399	1.409	1.8	2.0	2.0
3	1.417	1.373	1.395	–	4.4	–
3-Cr	1.439	1.388	1.414	1.9	5.1	0.7
<i>ex-4</i>	1.414	1.378	1.396	–	3.6	–
<i>ex-4-Cr</i>	1.438	1.390	1.414	1.8	4.8	1.2
<i>in-4</i>	1.449	1.356	1.403	–	9.3	–
<i>in-4-Cr</i>	1.461	1.377	1.419	1.6	8.4	–0.9
<i>ex-5</i>	1.411	1.382	1.397	–	2.9	–
<i>ex-5-Cr</i>	1.438	1.392	1.415	1.8	4.6	1.7
<i>in-5</i>	1.485	1.342	1.414	–	14.3	–
<i>in-5-Cr</i>	1.484	1.365	1.425	1.1	11.9	–2.4
	1.479	1.344	1.411	–0.3	13.5	–0.8
<i>in-5-Mo</i>	1.485	1.347	1.416	0.2	13.8	–0.5
<i>in-5-W</i>	1.480	1.356	1.418	0.4	12.4	–1.9

In contrast to the response of ΔQ , a clear monotonic relationship between the δ of the free arene, and $\Delta\delta$ between arene and (arene)metal complex is evident (*Fig. 2*). A linear regression of the data provides a best line with R^2 values of 0.98.

Previously, the X-ray crystal structures of a subset of the series' compounds have been published (*Table 3*) [23]. From their structural data, a correlation similar to that available from the computational data is found, albeit with greater scatter. For such subtle correlations, 'routine' crystal data can at best be corroborative. Without high-accuracy data, there is a great risk that the experimental error will obscure the effect. Here, we have the fortune of good agreement between theory and experiment, which provides a stronger case for the correlation. As an additional point, computations on **5-Mo** and **5-W** also show negative $\Delta\delta$ values (*cf. Table 2*). In combination with the

⁵) For the experimental synthesis and structure of **4** and **5**, see [22].

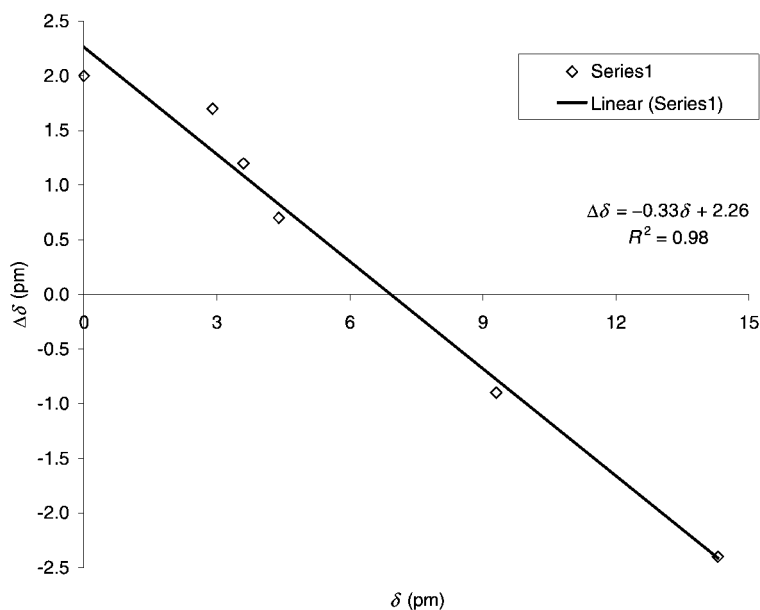


Fig. 2. Linearized plot of δ vs. $\Delta\delta$ for **1**, **3–5**, **1-Cr**, and **3-Cr to 5-Cr**

Table 3. X-Ray Structural Parameters for **1**, **3**, **4**, and Their $[\text{Cr}(\text{CO})_3]$ Complexes

Compound	<i>cis (endo)</i> [Å]	<i>trans (exo)</i> [Å]	<i>Q</i> [Å]	ΔQ [pm]	δ [pm]	$\Delta\delta$ [pm]
1	1.391	1.391	1.391	–	0	–
1-Cr	1.419	1.399	1.409	1.8	2.0	2.0
3	1.424	1.376	1.40	–	4.8	–
3-Cr	1.433	1.389	1.411	1.1	4.4	–0.4
<i>ex-4</i>	1.406	1.371	1.388	–	3.5	–
<i>ex-4-Cr</i>	1.429	1.381	1.405	1.7	4.7	1.2
<i>in-4</i>	1.449	1.349	1.399	–	10.0	–
<i>in-4-Cr</i>	1.456	1.375	1.415	1.6	8.1	–1.9

positive $\Delta\delta$ values for **1-Mo** and **1-W**, a similar correlation is suggested for all tricarbonyl (group VI metal) complexes.

The barrier to tricarbonylmetal rotation in these compounds also betrays aspects of the nature of the metal–arene interaction. As previously shown, **5-Cr** shows a substantial barrier to rotation about the metal–arene axis as evidenced by variable-temperature NMR studies (11.1 ± 0.5 kcal/mol). Earlier computations by means of HDFT gave satisfactory agreement with experiment (*ca.* 8 kcal/mol). In this study, *Hartree–Fock (HF)* and *HF* combined with *Møller–Plesset* perturbation theory (MP2) methods provided strikingly accurate values for the barrier (11.2 kcal/mol). The same levels of theory were applied to compute the rotational barrier in **5-Mo** and **5-W** and produced barriers of 15.2 and 13.6 kcal/mol, respectively. Looking to the geometry of the computed rotational transition states for **5-M** complexes, one finds that the ΔQ values are not essentially equivalent to those computed for the comparable

rotational ground states but are substantially less and in a manner proportional to the height of the computed rotational barrier. Such a pattern further supports the use of ΔQ as a gauge of the stability of metal–arene interaction in these complexes.

4. Discussion. – Benzene exemplifies aromaticity in its many faceted properties. Any modification of benzene is subject then to the question of whether this perturbed structure retains benzene-like (*i.e.*, aromatic) character. In the case of (arene)metal complexes, the early history shows extreme predictions such as those of *Ruch*, who claimed that bis(benzene)chromium should effectively represent bis(cyclohexatriene)chromium despite the possibility of D_{6h} symmetry [24]. On the flip side, the much-cited *Bailey* and *Dahl* structure for (benzene)tricarbonylchromium neglected the fact that C_{3v} is the maximum symmetry of the complex, and the authors concluded that the benzene ring remains six-fold symmetric [25]. These studies, at best, provided contrasting predictions about the effects of metal complexation on an arene's (specifically benzene's) state of delocalization.

Fortunately, high-accuracy structures on both systems corrected these early notions. In the context of our discussion, *Coppens* and *Rees* showed that the benzene ring of **1-Cr** adopts a staggered conformation with respect to the carbonyls and has a small but distinct bond-length alternation.

Albright, *Hofmann*, and *Hoffmann* provided an EHMO rationalization for the bonding in **1-Cr** [26] and predicted that the barrier to rotation of the tricarbonylmetal fragment would be very low (*ca.* 0.2 kcal/mol). They predicted that significant localization of the bonds in the arene should correlate with a substantially higher barrier to rotation⁶⁾. A general preference for the conformation with the carbonyl over the longer bond is consistent with an octahedral ligand field around the Cr-atom.

Chinn and *Hall* furthered this analysis to try to explain the general 'interruption of conjugation' in such (arene)metal complexes [28]. They acknowledged that the bond alternation occurs in an orientation that specifically eclipses the long bond with the carbonyl group. In these computations, they work from the fixed geometry from the X-ray structure and assume that geometric changes up to ± 5 pm would not have any appreciable effects on the results. They conclude that the three-fold distortion and the eclipsed orientation of the long bonds follow from the orbital analysis forwarded by *Albright et al.* [26]. The results presented here clearly contradict the assumptions of *Chin* and *Hall*. Within a difference of 5 pm in arene bond lengths, the distortions change from localizing to delocalizing, and, to our understanding, a single simple MO picture has not been presented to account for this effect.

Magueres, *Lindeman*, and *Kochi* noticed a similarity between the ΔQ values for (arene)metal complexes and radical-cation salts of similar arenes [29]. They asserted that the ΔQ values could be directly correlated to the degree to which the metal acted as an electron acceptor in such complexes. They also pointed to the similarity that carbonyl ligands in such complexes always eclipse the longer bonds of the arene. The trends in ΔQ found in this work also support the idea that the strength of metal–arene interaction, the degree/nature of ligand–metal electron transfer, and the value of ΔQ are related.

⁶⁾ For an experimental determination of the barrier to tricarbonyl chromium tripod rotation in **5-Cr**, see [27].

The use of a modified *Dewar–Chatt–Duncanson* model makes a clear structural prediction that the binding of a metal fragment to an isolated π system will elongate that π bond through a metalcyclopropanoid form; coordination of the metal removes density from the HOMO and donates back into the LUMO [30]. In simple olefins and polyenes, this is borne out.

It is our understanding of the treatment of *Albright et al.* [26] that a similar structural prediction applies to tricarbonylmetal complexes with benzene and cyclohexatriene. Indeed, if one considers the conformation of these complexes, the general rule that the carbonyl ligands eclipse the longer bond set in the arene evokes the conclusion that all of these complexes favor octahedral coordination. Although the end results appear the same, the path to the end point leads to very different conclusions about the influence of complexation on the bond localization of the arene.

As mentioned above, benzene's six-fold symmetry is not supported by the maximum symmetry of **1-Cr**. The bond-alternate structure found by *Coppens* and *Rees* thus evokes a conclusion from *Chinn* and *Hall* that metal complexation interrupts polyene conjugation. In contrast, the internal ring of **5** is a reasonable cyclohexatriene mimic and, in *in-5-Cr*, this cyclohexatriene mimic displays a substantially smaller degree of bond localization than that seen in **5**. Thus, one would conclude that, here, metal complexation enhances conjugation.

Most striking is the correlation between the degree of bond-length alternation in the starting arene and the change in that localization in the metal complex. Arenes that do not have the symmetry issues of benzene but that are highly delocalized (e.g., **3**, *ex-4*, and *ex-5*) become more localized by metal complexation. Beyond a certain limiting value of δ , there exist arenes with substantially enough localized character (e.g., *in-4* and *in-5*), such that the effect of metal complexation reverses, and their metal complexes display more delocalized character.

This correlation and the fact that, at its extremes, opposite effects occur with regard to the change in the geometric aromaticity of an arene upon metal complexation impinges directly on the studies of *Mitchell* and co-workers regarding the aromatic character in certain (arene)tricarbonylchromium complexes [31]. In *Mitchell's* analysis, the shift of the internal Me protons in 10b,10c-dimethyldihydro-10b,10c-dimethylpyrene (DHP) is used as a gauge of delocalization in the DHP annulene [32]. Fusing another ring to the DHP unit as in dihydrodimethylbenzpyrene (DHBP) allows one to see the effect of the fusion on the internal Me proton signals, and, in turn, one might deduce that these shifts are characteristic of how the fusion perturbs delocalization in the DHP unit. If one assumes that less delocalization in the DHP unit competes with delocalization in the fused ring system, then one could conclude from the internal Me shifts which ring system was more delocalized and hence more 'aromatic'. For a series of classical aromatic ring systems fused to DHP, the results follow what one would expect from classical assessments of aromaticity. Comparing the NMR shifts found for DHBP with those from the tricarbonylchromium complex of DHBP, and following the deductive scheme above, one would conclude that (benzene)tricarbonylchromium is more 'aromatic' than benzene (*i.e.*, superaromatic). *Mitchell* discusses this relative aromaticity effect as having two complementary components, the bond-directing power of the DHP and the bond-directing power of the fused ring system. In his analysis, it is presumed that greater bond fixation in the DHP implies a greater resistance to bond

fixation in the fused ring. Therein lies a caveat associated with that approach, one fully acknowledged by *Mitchell*.

Our interpretation of *Mitchell's* series of experiments is in line with *Mitchell's* later assessment that the NMR shifts report the power of the fused ring to localize the bonds in the DHP system, but we would argue that a fused ring system that itself was completely fixed could induce a fixed and oriented bond-length alternation in DHP. If the metal tripod fixed the bonds in the benzannulation or even just localized the bonding electrons to within the six-membered ring, then that could transmit a bond-localizing influence on the DHP such that the resonance contributors would no longer be comparable contributors, and from which the derived magnetic anisotropy would be diminished. Clearly, there will be cases in which the directing power of the fused ring will correspond to a greater resonance energy for the fused ring and, therefore, track with energetic criteria for aromaticity; however, the necessary condition to see the NMR signals of the Me groups shift is a stronger directing power of the fused ring system, not greater aromatic character of that ring. It does not make sense to us that a highly symmetric system, **1**, with equal bond lengths and in which the resonance forms per force of symmetry must be equal should be less delocalized (*i.e.*, aromatic) than a less-symmetric system, **1-Cr**, for which the resonance contributions cannot be equal. These arguments in combination with the induced bond-length alternation found in the crystal structure of **1-Cr** lead us to discount the relative aromaticity analysis in this case.

Recently, *Sorensen, Schleyer* and co-workers have also commented on the aromatic character of (benzene)tricarbonylchromium [33]. They conclude that **1-Cr** is not leaning towards antiaromatic in the arene, as *Simion* and *Sorenson* initially concluded [34], but rather is on par with the aromatic character of free benzene.

These discussions bring out the question of what we mean by the aromatic character of an arene in a complex. *Bursten* and *Fenske* have proposed that one can consider the (cyclobutadiene)iron complexes as 'aromatic' in a three-dimensional way [35]. However, it is unlikely that it was their intention to say the cyclobutadiene in such a complex could be taken out of context and called aromatic. Indeed, the very symmetry and orbital properties that make cyclobutadiene display anti-aromatic character are what allow it to interact so well with the carbonyliron fragment. Hence, it is the complex *in situ* that they are analyzing. So when *Simion* and *Sorensen* noted that the magnetic-susceptibility exaltation of **1-Cr** was less than for **1**, they were looking at the converse interaction seen by *Bursten* and *Fenske*. Analogously, it is the symmetry and orbital properties of benzene (the archetype of aromaticity) that allows the special properties of **1-Cr** to arise.

5. Conclusions. – The complexes formed by tricarbonylchromium and an arene display two subtle structure correlations with regard to the free arene. In all cases, the average bond length in the arene increases, and the magnitude of the increase can be an indicator of relative thermodynamic stability of the complex. Across the series **1, 3–5**, the degree of bond-length alternation in the free arene correlates with the direction and magnitude of the change in bond-length alternation in the tricarbonylmetal complex.

The increase in Q comes from a combination of bonding modes in which the metal 2e orbitals accept electron density from the HOMO e_{1g1} and e_{1g2} of benzene and the metal 1e orbitals back-donate electron density into the benzene LUMO e_{2u1} e_{2u2} . The

net interaction reduces the bonding within the π system in favor of stronger metal–arene interactions. Thus, ΔQ is a useful parameter for assessing metal–arene interactions.

The change in sign of $\Delta\delta$ is more difficult to explain. There appears to be an optimum degree of localization for a benzenoid ring to act as an η^6 -ligand within the octahedral ligand field for tricarbonylchromium. When the free arene is highly delocalized, then complexation localizes the bonds slightly. When the free arene is highly localized, then the metal binds to the three electron-rich π bonds, and the δ of the resulting arene is reduced. In both cases, it is reasonable to suggest a pseudo-*Jahn–Teller* effect that arises from the change in the E_u and E_g interaction as a function of metal complexation.

We would agree with others who have concluded that the total effect of metal complexation on the arene's 'aromaticity' is small, but note that any discussion of the aromaticity of an arene fragment carved out from such a metal complex is tenuous at best.

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