

A Theoretical Computation of the Aromaticity of (Benzene)Cr(CO)₃ Compared to Benzene Using the Exaltation of Magnetic Susceptibility Criterion and a Comparison of Calculated and Experimental NMR Chemical Shifts in These Compounds

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Abstract: A theoretical calculation of the aromaticity of benzene relative to (benzene)Cr(CO)₃ (**1**) based on the exaltation of magnetic susceptibility criterion was carried out using *ab initio* MO theory. As others have also found, benzene exhibits a diamagnetic susceptibility exaltation, $\Lambda_{\text{calc}} = -15.1$ ppm cgs, $\Lambda_{\text{exp}} = -13.7$ ppm cgs, and is aromatic. In contrast, (benzene)Cr(CO)₃ (**1**) has a positive susceptibility exaltation, $\Lambda_{\text{calc}} = 12.3$ ppm cgs, characteristic of an antiaromatic compound. The validity of susceptibility exaltation as an aromaticity indicator for organometallic compounds was also tested for (cyclobutadiene)Fe(CO)₃ (**16**), which proved to be aromatic ($\Lambda_{\text{calc}} = -6.10$ ppm cgs). The validity of the calculations was further supported by a comparison of the calculated isotropic susceptibility χ_{av} of **1** (-109.3 ppm cgs) with an experimental result (-113 ± 22 ppm cgs). The related NMR calculations for **1** reproduce very well the ¹³C solid state results of Waugh and also the experimental isotropic upfield shift of ca. 2 ppm seen in the ¹H NMR spectra of complex **1** relative to benzene. Contrary to the usual assumptions, the in-plane shieldings of the complexed benzene ring are more important than the perpendicular (ring current) counterparts. As expected, the present theoretical study reproduces very well the experimental geometries, energies, and harmonic frequencies of the purely organic compounds, but there is also very good agreement in the calculated properties of the organometallic compounds, where such data are available for comparison. The present study is based on GIAO, CSGT, and IGAIM NMR calculations performed on the optimized geometry of the most stable conformation at the B3LYP/6-311+G** level for the 12 organic and organometallic compounds needed directly or indirectly for the “group increment” magnetic susceptibility exaltation determinations. The organometallic structures include Cr(CO)₆ (**10**), (ethylene)Cr(CO)₅ (**11**), (1,3-butadiene)Cr(CO)₄ (**12**), (benzene)Cr(CO)₃ (**1**), Fe(CO)₅ (**13**), (ethylene)Fe(CO)₄ (**14**), (1,3-butadiene)Fe(CO)₃ (**15**), and (cyclobutadiene)Fe(CO)₃ (**16**).

1. Introduction

Benzene can be complexed to Cr(CO)₃ to give the very well-known compound (benzene)Cr(CO)₃ (**1**), and in this complex the benzene fragment becomes significantly changed relative to free benzene. This includes (i) geometry changes, (ii) electronic changes, mainly involving net electron withdrawal by the metal, (iii) upfield shifts in both ¹H and ¹³C NMR peaks, and (iv) a recent estimate that the resonance energy of the complex exceeds that of free benzene.¹

We are particularly interested in the latter two features since there has been much controversy concerning the origin of the NMR changes, and there is continuing interest in the aromaticity–resonance energy question, both of itself and as a possible explanation of the NMR changes, i.e. through ring current effects. This paper reports a high-level *ab initio* MO calculation of (benzene)Cr(CO)₃, in which we have focused on the aromaticity question by calculating various magnetic properties of the system.

A characteristic feature of the ¹H-NMR spectrum of the (benzene)Cr(CO)₃ complex (**1**) is that the arene protons resonate at significantly higher (ca. 2 ppm) fields than in the free benzene (**2**). This upfield shift has prompted much investigation of its origin.^{2–6} Such shifts have been interpreted as a combination

of effects including quenching of the ring current, increase of electron density on the aromatic ring, the magnetic anisotropy of the chromium ligand bond, and partial sp²–sp³ rehybridization of the ring carbon atoms. It has proven conceptually difficult to even separate some of these contributions.

Early ¹H-NMR studies of various para-substituted complexes indicated that the chromium tricarbonyl group exerts a levelling effect on the distribution of electron density in the arene ligand.⁷ More recently, the chemical shifts of the amino protons of para-substituted aniline complexes have been shown to correlate well with the substituent σ or σ^- constants, indicating the retention of direct resonance interaction between the substituents and the amino nitrogen.⁸ However, the slope ρ is markedly smaller than that found for the free X-C₆H₄-NH₂ compounds. This reduction in the sensitivity to substituent effects was rationalized in terms of strong electron withdrawal by the Cr(CO)₃ group, inducing a buffering positive charge on the complexed arene ring.

As in ¹H NMR, coordination to the Cr(CO)₃ moiety causes a large upfield shift in the ¹³C resonance of arene carbon atoms

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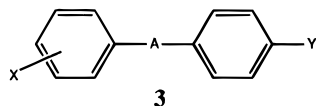
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(e.g. 35 ppm for benzene^{9,10}). This upfield shift has been variously attributed to several effects, including those already discussed above for ¹H-NMR resonances, and there is no complete consensus on this.¹¹ A recent solid state ¹³C-NMR study of [Cr(CO)₃(η⁶-arene)] (arene = C₆H₆, C₆Me₆, C₆Et₆) reveals a marked directional character to the shielding.¹² The upfield shift is almost entirely accounted for by a very large (>50 ppm) specific increase in the shielding when the external magnetic field lies in the plane of the aromatic ring along the bonds to the substituents.

Interestingly, an analysis of the C(4) chemical shifts of both free and complexed arenes in the series [Cr(CO)₃(η⁶-XC₆H₅)] (X = H, F, Cl, Me, MeO, COMe, NH₂, NMe₂, etc.) shows no significant change in the transmission of resonance substituent effects upon complexation. This implies little or no disturbance of the π-system. In contrast, the C(1) chemical shifts for the complexed arenes show^{13,14} a much greater sensitivity to the one-bond inductive substituent effects than do free arenes. This observation, together with the increase in ¹J(¹³C-¹H) coupling constants upon complexation, is consistent with a net withdrawal of electron density by the Cr(CO)₃ fragment from the σ-framework of the arene ring. Similar conclusions have been drawn from ¹³C-NMR studies of polyaromatic species of the type **3**.¹⁵ Further support for electron withdrawal by Cr(CO)₃ via predominantly σ- rather than π-interactions comes from a ¹⁹F-NMR investigation of the *p*-fluoroarene complexes [Cr(CO)₃(η⁶-XC₆H₄F)] (X = 3- or 4-H, F, Cl, Me, MeO, NH₂, CF₃).¹⁶ The transmission of resonance effects (by para substituents) within the ring was found to differ little in the free and complexed arenes, whereas the transmission inductive effects (of meta substituents) were greatly diminished.



A = CH₂, C₂H₄, C₂H₂, CO, or absent
X, Y = various H, F, Cl, Me

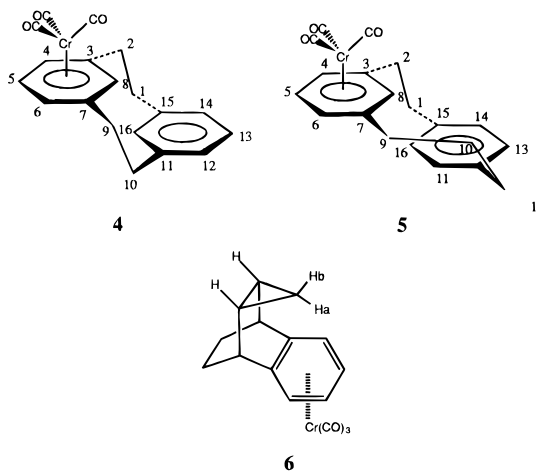
The preceding ¹H-, ¹³C-, and ¹⁹F-NMR results do not directly address the question of the aromaticity of the complexed benzene ring but they do provide evidence that the chromium withdraws electrons from both the benzene π and σ bonds, if indeed one can separate these effects.

An obviously sensitive probe of any modification of the arene π-system on complexation would be the measurement of possible changes in "ring current". The idea that the "magnetic anomaly" (i.e. a stronger diamagnetic susceptibility than expected from additivity rules such as those of Pascal,¹⁷ together with a pronounced anisotropy of the susceptibility, and a deshielding of the protons attached to the ring carbons) is due to ring currents in the π-electron system is relatively old.¹⁸ The first quantum mechanical treatment on the level of Hückel theory was reported by London,¹⁹ in which he also introduced the

concept of gauge invariant (or gauge including) orbitals (GIAO's). Soon after the difference in the proton magnetic shielding between benzene and monocyclic olefins was observed,²⁰ a rationalization in terms of the ring current model was given by Pople,²¹ who has also made further contributions to the topic.^{22,23} The ring current model has been very successful but there has also been criticism, and some modifications have been suggested. The state of affairs in 1980, i.e. before the advent of powerful *ab initio* methods for the calculation of magnetic susceptibilities and chemical shifts, has been reviewed by Haig and Mallion.¹⁸

Recently the Kutzelnigg and Lazzeretti groups have performed coupled Hartree-Fock-IGLO²⁴ computations of magnetic susceptibility tensors for benzene, hypothetical cyclohexatriene, and some isomers of benzene, as well as other olefins. While the papers of Lazzeretti *et al.*^{25,26} have reservations about the classical ring current picture, the study of Kutzelnigg²⁴ was rather consistent with this model. These differing conclusions were to some extent based on different interpretations of what the London model should imply. The two groups concluded that "the more literally one takes it [ring current model], the less confirmation from a rigorous study will result", a sort of Uncertainty Principle statement.

Two NMR studies have been constructed to test experimentally the ring current disruption hypothesis.^{27,28} In the first one, the chemical shift difference (Δδ) between the monitor proton H(16) and H(12) in the [2.2]metacyclophane complex **4** reflects the shielding influence of the Cr(CO)₃ coordinated arene. The observed smaller value of Δδ compared with that found in the corresponding free [2.2]metacyclophane was interpreted as meaning that the ring current shielding is considerably reduced below the plane of the coordinated ring. Similar evidence for ring current disruption comes from monitoring the chemical shifts of protons H(14) and H(16) in the [2.2]metaparacyclophane complex **5** and free arene. Furthermore, the geometry of the ligand was shown to be preserved upon complexation in each of the above systems (by examining the H(8) protons).



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In the second study the ¹H-NMR properties of tricarbonyl(η⁶-[8]paracyclophane)chromium(0)²⁸ were also consistent with a decrease in ring current upon complexation with Cr(CO)₃, but a recent paper²⁹ has shown that there is a strong solvent dependence of the ¹H-NMR chemical shifts which limits an assessment of the degree of quenching of the aromatic ring current due to the η⁶-complexation.

In contrast, employing complex **6** and the corresponding free barralene as models (monitor protons H_a and H_b), another study concluded that there is general preservation of the ring current upon complexation.³⁰

One can conclude from the above studies that there is still controversy surrounding the interpretation of the comparative ¹H shifts in coordinated and free arenes, but on balance there is some indication that "ring currents" are diminished in the complexes.

A totally unrelated approach to this whole topic is to be found in a very recent study by Mitchell *et al.*^{1,31} These authors have evaluated the "bond-fixing" properties of a number of aromatic systems side-fused to a 14 π-electron aromatic dihydropyrene skeleton. They have been able to quantify this "bond-fixation" criterion with known values for aromatic resonance energy, and using this protocol, (benzene)Cr(CO)₃ (**1**) was evaluated as 1.3 times *more* aromatic than benzene (**2**)!

In trying to reconcile all of these somewhat disparate literature results, we were attracted by the recent theoretical work of Kutzelnigg^{24,32–35} and Schleyer^{36–41} In work from about 30 years ago, Dauben^{42–44} proposed a criterion for aromaticity based on the calculation of an "exaltation of magnetic susceptibility" Λ, derived by a group increment approach in which one compares the expected magnetic susceptibility for the localized π-electron system with that measured experimentally for the "real" system. For an aromatic ring Λ is negative (diamagnetic), and for an antiaromatic ring it is positive. However, for many interesting systems, including (arene)Cr(CO)₃ compounds, there is no experimental magnetic data on some of the molecules which one wants for the group increments. Indeed one of these latter molecules (1,3-butadiene)-Cr(CO)₄ (**12**) has not yet been reported. Kutzelnigg²⁴ and more recently Schleyer^{36–41} have shown that magnetic susceptibilities can now be calculated to reasonable accuracy for molecules of interest to organic and inorganic chemists.

The primary objective of this study was to calculate and compare magnetic susceptibility exaltations for benzene (**2**) and

(benzene)Cr(CO)₃ (**1**). Since the high-level computation of transition-metal organometallics is in its infancy, we have also spent considerable time in verifying that our theoretical methods give reasonable results for quantities other than magnetic susceptibility, e.g. geometry and vibrational frequencies. Also, the accuracy of the susceptibility calculations can be independently evaluated by comparison of calculated and experimental NMR chemical shift data and with data on the anisotropy of shielding tensors derived from solid-state NMR results.

One could argue that the relatively simple "group increments" approach needed for computing the benzene exaltation of magnetic susceptibility might be suspect in the case of a three-dimensional molecule such as the Cr(CO)₃ complex. We have therefore also carried out, for comparison purposes, an exaltation calculation of (cyclobutadiene)Fe(CO)₃, which is widely regarded as aromatic.

2. Method and Basis Sets

All *ab initio* calculations were performed with the GAUSSIAN 94 program⁴⁵ on a Silicon Graphics work station, using the Becke3LYP hybrid method^{46–51} which includes a mixture of Hartree–Fock exchange with DFT exchange-correlation.

All calculations were done with a 6-311+G** internal basis set which specifies the 6-311G basis for first-row atoms, the MacLean–Chandler (12s,9p)-(621111,52111) basis sets for second-row atoms,^{52,53} and the Wachters–Hay^{54,55} all electron basis set for the first transition row, using the scaling factors of Raghavachari and Trucks,⁵⁶ augmented by polarization and diffuse functions.^{57,58}

Geometries were optimized in the most stable conformation and characterized by frequency analysis. Energies have been corrected for ZPVE.

The NMR shielding tensors were computed with four different methods: (i) the Gauge-Independent Atomic Orbital (GIAO),^{59–62} (ii) the Continuous Set of Gauge Transformations (CSGT),^{63,64} (iii) the IGAIM⁶⁴ method (a slight variation on CSGT which use atomic centers as gauge origin), and (iv) the Single Origin method. Chemical shifts were obtained in parts per million relative to the absolute shielding constant (σ) of TMS (*T_d*, B3LYP/6-311+G**).

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IGAIM, and Single Origin methods, and the units used are the same as those recently described by Kutzelnigg.²⁴

3. Results and Discussion

There is voluminous primary data generated in these calculations (energies, geometries, harmonic frequencies, NMR shieldings (chemical shifts), and magnetic susceptibilities). We have chosen to put much of this in the supporting information, but it is important to verify the quality of the calculation by making some comparisons to experimental data, where this is available.

For compounds **1** and **10** and later for **13–16**, calculated and experimental geometries are listed in Tables 1 and 5. The calculated and experimental ¹H and ¹³C NMR data are given in the supporting information (Table 11 for compounds **1**, **2**, and **7–12** and Table 12 for compounds **13–16**) but a graphical plot of the calculated data *vs* experimental values is shown in Figures 3, 4, 6, and 7 with an overall good correlation. Energies are given as supporting information (Table 8) since there is very little experimental comparison that can be made. Harmonic frequencies and the experimental values are also presented as supporting information (Tables 9 and 10), except for a graphical comparison of calculated and experimental values for (benzene)Cr(CO)₃ given in Figure 2. A complete listing of magnetic susceptibilities is given in Tables 4 and 6.

A. Magnetic Calculations for the Evaluation of Benzene and (Benzene)Cr(CO)₃ Aromaticity and Their Use in Rationalizing NMR Chemical Shift Changes. The magnetic susceptibility exaltation [Λ , eq 1] is defined as the difference between the computed magnetic susceptibility (χ_M) for the observed compound [(benzene)Cr(CO)₃, (**1**)] and the value estimated for the hypothetical system without cyclic electron delocalization (χ'_M). The latter is based on the bond increments that we have determined by computations on appropriate model compounds (for the derivation see Appendix). The exaltations Λ are negative (diamagnetic) for aromatic compounds, but positive (paramagnetic) for the antiaromatic cases.

$$\Lambda = \chi_M - \chi'_M \quad (1)$$

The structural formulas of the molecules of interest to this section are shown in Figure 1 together with the symmetry and the numbering of the atoms. These are ethylene (**7**), s-trans-butadiene (**8**), s-cis-butadiene (**9**), benzene (**2**), Cr(CO)₆ (**10**), (ethylene)Cr(CO)₅ (**11**), (butadiene)Cr(CO)₄ (**12**), and (benzene)Cr(CO)₃ (**1**).

Selected calculated (B3LYP/6-311+G**) and experimental geometric parameters for structures **1** and **10** are presented in Table 1. Our primary concern in the computations was with the known difficulties associated with a proper description of a carbon–metal bond. The gas-phase structure of (benzene)Cr(CO)₃ (**1**) has recently been determined by Kukolich *et al.*⁶⁵ from a microwave spectrum, but there is a bond length uncertainty of ± 0.01 – 0.02 Å. An earlier electron diffraction measurement by Chiu *et al.*⁶⁶ found six equivalent C–C bonds at 400 K, suggesting free internal rotation at this temperature. The best agreement with our calculations comes from the solid-state structure of (benzene)Cr(CO)₃ (**1**) (Table 1), where the difference between the two distinct types of C–C bonds is well reproduced. The calculated Cr–C_{carbonyl} distance is slightly too long compared to solid-state data. However, this bond length is somewhat longer by the gas-phase experiments: 1.86 Å⁶⁵ and 1.863 Å,⁶⁶ which both compare well with the calculated

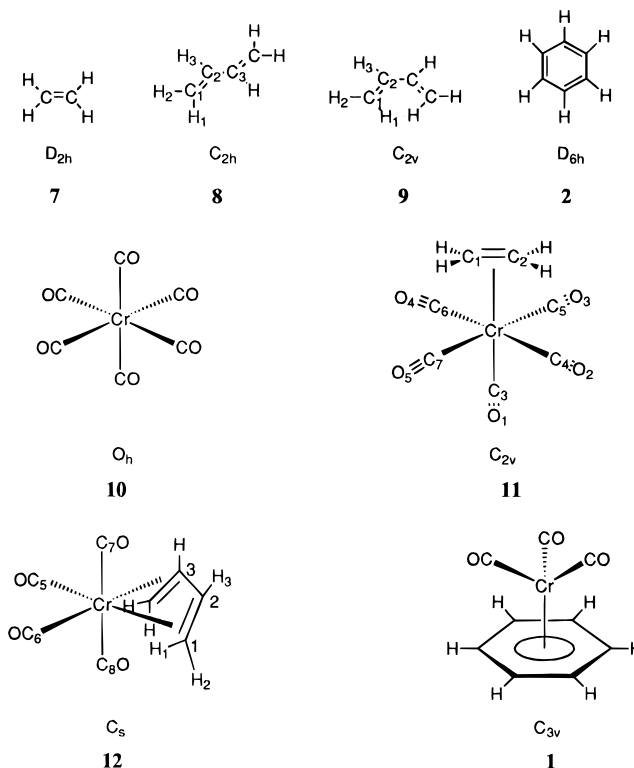


Figure 1. Structural formulas, symmetry, and numbering of atoms for the molecules used in the group increment calculations involving **1** and **2**.

Table 1. Calculated^a and Experimental Geometric Parameters for Structures **1** and **10**

| bond length (Å) or angle (deg) | calcd | expt |
|---|--------|---------------------|
| Cr(CO) ₆ (<i>O_h</i>) (10) | | |
| Cr–C | 1.927 | 1.918 ^b |
| C–O | 1.141 | 1.141 |
| (benzene)Cr(CO) ₃ (<i>C_{3v}</i>) (1) | | |
| Cr–C _{ring} | 2.247 | 2.223 ^c |
| Cr–C _{carbonyl} | 1.860 | 1.845 |
| C–O | 1.153 | 1.159, 1.157 |
| C–C | 1.402 | 1.406, 1.407 |
| C–C ^d | 1.421 | 1.424, 1.422 |
| C–H | 1.082 | 1.106, 1.113, 1.109 |
| Cr–C–O | 181.26 | 177.9, 178.5 |
| C _{carbonyl} –Cr–C _{carbonyl} | 89.29 | 89.14, 86.37 |
| C–C–C | 120.0 | 120.0, 119.8, 120.1 |
| C–C–H | 120.5 | 119.72 |
| H's tilt toward Cr | 2.6 | 1.7 |

^a B3LYP/6-311+G**. ^b Neutron diffraction solid state data from: Jost, A.; Rees, B.; Yelon, W. B. *Acta Crystallogr.* **1975**, *B31*, 2649. ^c Neutron diffraction solid state data from: Rees, B.; Coppens, P. *Acta Crystallogr.* **1973**, *B29*, 2515. ^d C–C bisected by the Cr–CO bond.

1.860 Å value. The calculated Cr–C_{ring} distances are slightly too long compared to the solid-state values, while the C–O distances are well reproduced for both (benzene)Cr(CO)₃ (**1**) and Cr(CO)₆ (**10**). The benzene ring maintains the planarity of the carbon framework, and all hydrogen atoms are equally tilted toward the metal by 2.6°. The direction and magnitude of the hydrogen tilt agrees well with the experimental observations.

The frequency data for compounds **1**, **2**, and **7–12** were compared where possible with experimental data (see supporting information, Tables 9 and 10). The results for (benzene)Cr(CO)₃ are particularly cogent and are shown as a graphical representation in Figure 2.

Finally, we comment on the magnetic properties, the main rationale for this study. Among the four different NMR

(65) Kucolich, S. G.; Sickafoose, S. M.; Flores, L. D.; Breckenridge, S. M. *J. Chem. Phys.* **1994**, *100*, 6125.

(66) Chiu, N. S.; Schäfer, L.; Seip, R. J. *Organomet. Chem.* **1975**, *101*, 331.

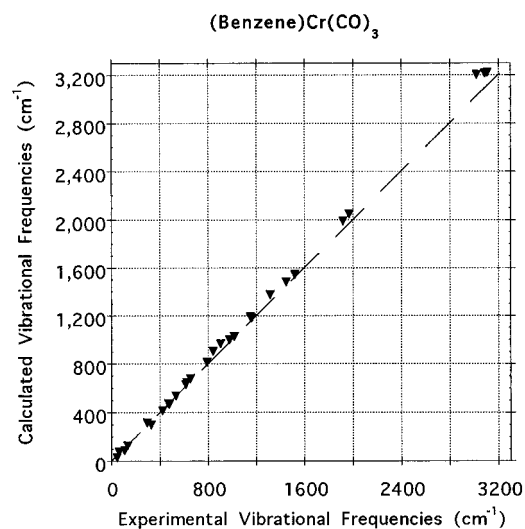


Figure 2. Calculated (B3LYP/6-311+G**//B3LYP/6-311+G**) vs experimental harmonic frequencies for (benzene)Cr(CO)₃.

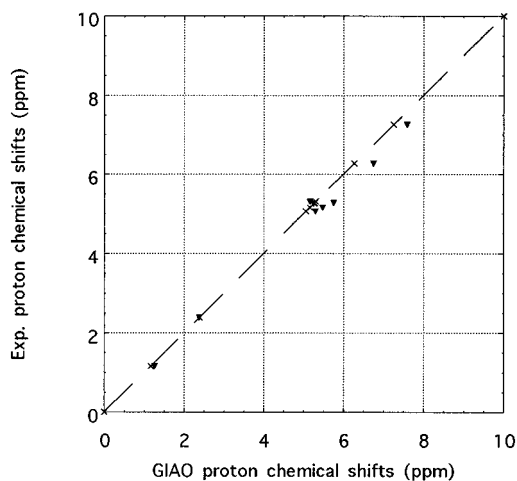


Figure 3. Calculated (GIAO/B3LYP/6-311+G**//B3LYP/6-311+G**) vs experimental ¹H chemical shifts (ppm) for compounds **1**, **2**, and **7–12**.

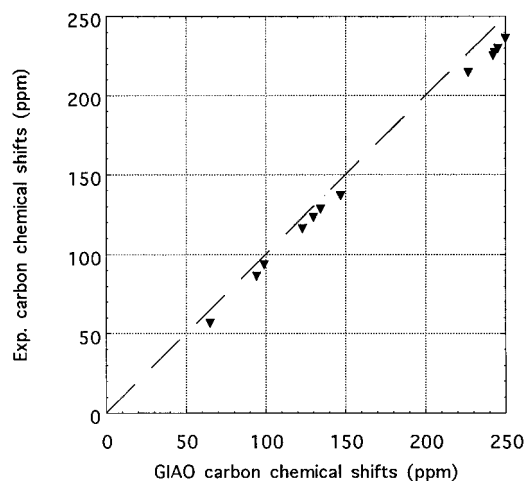


Figure 4. Calculated (GIAO/B3LYP/6-311+G**//B3LYP/6-311+G**) vs experimental ¹³C chemical shifts (ppm) for compounds **1**, **2**, and **7–12**.

programs available in the GAUSSIAN 94 package, the Gauge-Independent Atomic Orbital (GIAO)^{59–62} method gives the best results for the NMR chemical shifts (see the graphical representations in Figures 3 and 4). The Continuous Set of Gauge Transformations (CSGT)^{63,64} and the IGAIM⁶⁴ methods give, as expected, results similar to each other. They are individually

Table 2. A Comparison of Calculated^a vs Experimental^b Anisotropic ¹³C Shielding Parameters^c for Benzene^d and (Benzene)Cr(CO)₃^d

| compd | σ_{ip} | $\sigma_{zz(L)}$ | $\Delta(\sigma_{ip})^e$ | $\Delta(\sigma_{zz(L)})^e$ |
|------------------------------------|---------------|------------------|-------------------------|----------------------------|
| benzene calcd | -61.47 | 122.90 | | |
| (benzene)Cr(CO) ₃ calcd | -13.77 | 128.23 | +47.7 | +5.3 |
| (benzene)Cr(CO) ₃ exptl | -16 | 122 | +44 | +2 |

^a IGAIM/B3LYP/6-311+G**//B3LYP/6-311+G**. ^b Reference 12. ^c Experimental anisotropic σ values are relative to the experimental isotropic σ value for benzene (ppm). For comparison purposes, our calculated anisotropic σ values are also relative to the calculated isotropic σ value for benzene (ppm). ^d For both benzene and (benzene)Cr(CO)₃, the z -axis is perpendicular to the arene ring, generating $\sigma_{zz(L)}$ shielding values. For (benzene)Cr(CO)₃, the standard orientation for the x and y axes used in the calculation differs from that used in the experimental work. Therefore we quote only a $\sigma_{ip} = (\sigma_{xx} + \sigma_{yy})/2$, as an axis-independent average of the in-plane σ components. ^e The change in the shielding value on going from benzene to the Cr(CO)₃ complex.

Table 3. Calculated ¹H NMR Shielding Parameters^a for Benzene and (Benzene)Cr(CO)₃

| compd | σ_{zz} | $\sigma_{ip} = (\sigma_{xx} + \sigma_{yy})/2$ | $\sigma_{isotropic}$ |
|------------------------------|---------------|---|----------------------|
| benzene | 21.60 | 25.52 | 24.22 |
| (benzene)Cr(CO) ₃ | 22.64 | 28.23 | 26.37 |
| net change on complexation | +1.04 | +2.71 | +2.15 |
| experimental | | | +1.95 |

^a Absolute values in ppm using IGAIM/B3LYP/6-311+G**//B3LYP/6-311+G**.

less accurate than the GIAO values (supporting information, Table 11), but follow the experimental trends reasonably well. The Single Origin method (SGO) results are not listed, since this calculation gives very poor agreement with experiment.

The NMR programs are able to reproduce not only the isotropic average of the shielding tensor but also its anisotropy. A component analysis of the ¹³C shielding elements for the ring-carbon atoms in benzene (**2**) and (benzene)Cr(CO)₃ (**1**) to determine the effects of complexation is shown in Table 2. In this table, the experimental results of Waugh et al.¹² are compared to the calculated values. The computed $\Delta\sigma$ results, which are within ± 5 ppm of the experimental determination, agree with the experimental finding that the change in ¹³C chemical shifts observed on complexation is almost entirely accounted for by a large change (>44 ppm) in the shielding when the external field is in the plane of the benzene ring in a radial direction (i.e. the in-plane elements σ_{ip} are more affected upon complexation than the perpendicular element σ_{zz}). It is noteworthy that the lowest energy electronic transition in (benzene)Cr(CO)₃ has been calculated to be a $5e \rightarrow 6e$ transition and to be xy polarized.⁶⁷ One can view the above shielding as requiring enhanced electron circulation about an axis parallel to the C–H bond, and this argument can in turn be used to partially explain the marked 2 ppm upfield shift of the aromatic protons upon complexation. In Table 3, we have listed the calculated ¹H-NMR shielding parameters for benzene and (benzene)Cr(CO)₃. The upfield NMR shift in the complex compared to benzene is computed as 2.15 ppm, quite close to the experimental value of 1.95. This upfield shift comes from an increase in both the σ_{zz} and σ_{ip} shieldings, with the latter the larger value. The increased value of the σ_{zz} component could be described in terms of a *decreased* ring current in the complex, but this comparison ignores any properties of the Cr(CO)₃ group itself. As mentioned earlier, this upfield shift on complexation has often been attributed to a quenching of the aromatic ring current,⁶⁸ but our calculations show that this could only be a

(67) Caroll, D. G.; McGlynn, S. P. *Inorg. Chem.* **1968**, *7*, 1285.

(68) Strohmeier, W.; Hellman, H. *Chem. Ber.* **1964**, *97*, 1877.

Table 4. Magnetic Susceptibility Data (ppm cgs with sign reversed) for Compounds **1**, **2**, and **7–12**

| compd | CSTG or IGAIM ^a | | | | | IGLO ^f | | exptl | |
|---|----------------------------|--------------|--------------|---------------|----------------|-------------------|----------------|---------------|-----------------------|
| | ϵ_1^b | ϵ_2 | ϵ_3 | χ_{av}^c | $\Delta\chi^d$ | χ_{av}^c | $\Delta\chi^e$ | χ_{av}^c | $\Delta\chi^e$ |
| C ₂ H ₄ (7) | 22.47 | 14.38 | 14.38 | 17.08 | -4.0 | 22.5 | | | |
| <i>s-trans</i> -1,3-butadiene (8) | 38.82 | 26.01 | 22.96 | 29.26 | -9.4 | 40.5 | | | |
| <i>s-cis</i> -1,3-butadiene (9) | 41.20 | 25.59 | 23.49 | 30.0 | -9.9 | 39.5 | | | |
| benzene (2) | 97.88 | 30.41 | 30.41 | 52.9 | -33.7 | 67.5 ^e | 67.4 | 61.8 | 54.8 ^g |
| Cr(CO) ₆ (10) | 82.93 | 82.93 | 82.93 | 82.9 | 0 | | | | 10 ⁱ |
| (C ₂ H ₂)Cr(CO) ₅ (11) | 101.9 | 89.10 | 80.00 | 90.3 | -15.5 | | | | |
| (1,3-butadiene)Cr(CO) ₄ (12) | 118.3 | 108.7 | 82.67 | 103.2 | -30.8 | | | | |
| (benzene)Cr(CO) ₃ (1) | 135.7 | 96.10 | 96.10 | 109.3 | -19.8 | | | | 113 ± 22 ^j |

^a Both methods give the same values. ^b $\epsilon_1, \epsilon_2, \epsilon_3$: eigenvalues of the magnetic susceptibility tensor as reported in the Gaussian 94 output file (where arbitrarily $\epsilon_1 < \epsilon_2 < \epsilon_3$). ^c χ_{av} is the isotropic part [$\chi_{av} = 1/3(\epsilon_1 + \epsilon_2 + \epsilon_3)$] or defined in terms of in-plane ($\chi_{xx} + \chi_{yy}$) and out-of-plane (χ_{zz}) components [$\chi_{av} = 1/3(\chi_{xx} + \chi_{yy} + \chi_{zz})$]. ^d $\Delta\chi$ is the anisotropic part [$\Delta\chi = \epsilon_3 - (\epsilon_2 + \epsilon_1)/2$]. ^e For molecules like benzene where in-plane and out-of-plane χ components are easily identified, $\Delta\chi$ is usually reported as [$\Delta\chi = \chi_{zz} - (\chi_{xx} + \chi_{yy})/2$]. This is the definition used in the experimental work. ^f Reference 24. ^g Hoarau, J.; Lumbroso, N.; Pacult, N. *C. R. Acad. Sci.* **1956**, *242*, 1702. ^h Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653. ⁱ Klemm, W.; Jacobi, H.; Tilk, W. *Z. Anorg. Chem.* **1931**, *201*, 17. This result would appear to be in error. ^j Fischer, E. O.; Joos, G.; Meer, W. *Z. Naturforsch.* **1958**, *13b*, 456.

minor factor. Kutzelnigg *et al.*,²⁴ using IGLO calculations, have shown that ring currents affect the magnetic susceptibility of benzene strongly (mainly its anisotropy) but have arguably only a small effect on the ¹H and ¹³C chemical shifts, and their analysis on this subject should also be kept in mind when discussing the properties of **1**. Our IGAIM and CSGT calculations on benzene give similar results to the older IGLO calculations.²⁴

The computed (CSGT, IGAIM) and experimental magnetic susceptibilities are collected in Table 4 together with some IGLO results for the non-metallic compounds as reported by Kutzelnigg *et al.*²⁴ In Table 4 we list the eigenvalues of the magnetic susceptibility tensor as well as the isotropic part χ_{av} and the anisotropy $\Delta\chi$. There is good agreement between the experimental χ_{av} value for both benzene (**2**) and (benzene)Cr(CO)₃ (**1**) and the values calculated in this study using CSGT and IGAIM procedures.

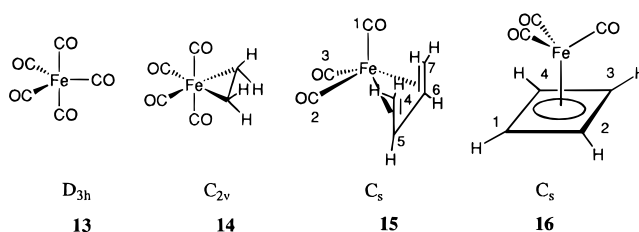
The magnetic susceptibility data presented in Table 4 include all of the molecules needed for the increments involved in calculating χ_{av} (see Appendix) for hypothetical cyclohexatriene and (cyclohexatriene)Cr(CO)₃. From this increment system one predicts $\chi'_{av} = -37.79$ ppm cgs for cyclohexatriene and $\chi'_{av} = -121.64$ ppm cgs for (cyclohexatriene)Cr(CO)₃. Consequently the magnetic susceptibility exaltation for the two compounds will be:

$$\Lambda(\text{benzene}) = \chi_{av}(\text{benzene}) - \chi'_{av}(\text{cyclohexatriene}) = -52.89 - (-37.79) = -15.1 \text{ ppm cgs}$$

$$\Lambda[(\text{benzene})\text{Cr}(\text{CO})_3] = \chi_{av}[(\text{benzene})\text{Cr}(\text{CO})_3] - \chi'_{av}[(\text{cyclohexatriene})\text{Cr}(\text{CO})_3] = -109.31 - (-121.64) = 12.33 \text{ ppm cgs}$$

Whereas benzene (**2**) has a negative value of -15.1 ppm cgs (in good agreement with the -13.7 ppm cgs value reported by Dauben *et al.*⁴⁴), and is of course aromatic, (benzene)Cr(CO)₃ (**1**) has a positive exaltation characteristic of antiaromatic compounds.

B. Magnetic Criteria for Evaluations of (Cyclobutadiene)Fe(CO)₃ Aromaticity. Although the "group increments" approach is designed to add and subtract bonds of the same type, there are more unknowns when one applies this procedure to organometallics than to systems like benzene itself. Consequently we have sought to apply this exaltation of magnetic susceptibility criterion for aromaticity to another organometallic, choosing the case of (cyclobutadiene)Fe(CO)₃. This organometallic is widely recognized as being aromatic and the concept

**Figure 5.** Structural formulas, symmetry, and number of atoms for the molecules used in the group increment calculations involving **16**.

of "metalloaromaticity" has been introduced⁶⁹ to account for the remarkable properties of this compound.

The magnetic susceptibility for the hypothetical system without cyclic electron delocalization (χ'_M) was calculated in the same way as for (benzene)Cr(CO)₃, from bond increments that were determined by computations on appropriate model compounds (for the derivation see Appendix).

The structural formulas of the required molecules are shown in Figure 5 together with the symmetry and the numbering of the atoms. These are the following: iron pentacarbonyl (**13**), (ethylene)Fe(CO)₄ (**14**), (butadiene)Fe(CO)₃ (**15**), and (cyclobutadiene)Fe(CO)₃ (**16**).

Selected calculated and experimental geometric parameters for structures **13–16** are presented in Table 5.

The geometry of Fe(CO)₅ (**13**) is essentially trigonal bipyramidal, but there has been some debate as to whether the Fe-C_(equatorial) and Fe-C_(axial) bond lengths differ significantly.⁷⁰ The most recent gas-phase electron diffraction results on Fe(CO)₅ indicate that the equatorial Fe-C bond distance is longer by 0.020(6) Å.⁷¹ A very accurate X-ray diffraction study reveals that the axial and equatorial Fe-C bond distances are equal to within the uncertainty arising from distortion of the equatorial bonds by solid-state packing effects, ±0.003 Å.⁷² Our computational results have the axial Fe-C bonds longer than equatorial by 0.007 Å, but in absolute terms the calculations give a very good account of experimental bond lengths.

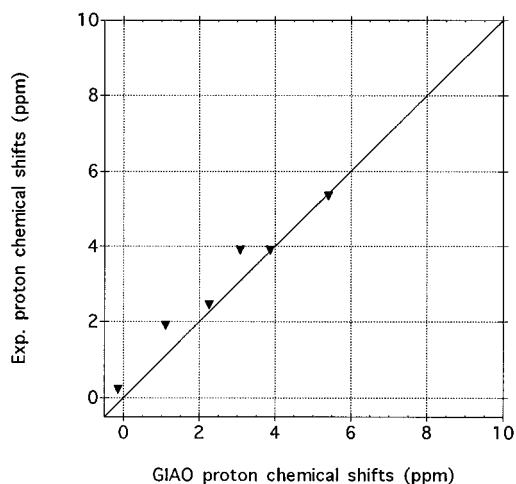
All known structures of complexes of the type (alkene)Fe(CO)₄ are based on a trigonal bipyramid and may be regarded as derived from Fe(CO)₅ by replacing one equatorial CO group by an alkene, with the C=C bond aligned in the equatorial plane. The calculation fails to predict the difference between axial and equatorial Fe-C bond lengths and overestimates the Fe-

(69) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760.(70) Jones, L. H.; McDowell, R. S.; Goldblatt, M.; Swanson, B. I. *J. Chem. Phys.* **1972**, *57*, 2050.(71) Burnvoll, J. *Acta Chem. Scand.* **1967**, *21*, 1390.(72) Donohue, J.; Caron, A. *Acta Crystallogr.* **1964**, *17*, 663.

Table 5. Calculated and Experimental Geometric Parameters for Structures Shown in Figure 5

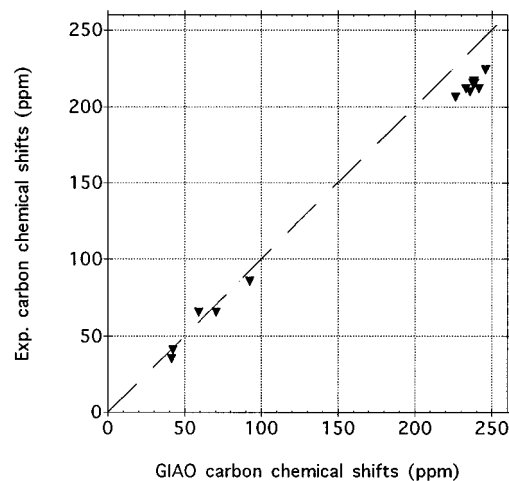
| bond length (Å) | calcd ^a | exptl |
|---|--------------------|---|
| Fe(CO) ₅ (<i>D</i> _{3h}) (13) | | |
| Fe–CO _{ax} | 1.828 | 1.807 ^b |
| Fe–CO _{eq} | 1.821 | 1.827 |
| (C–O) _{ax} | 1.139 | 1.152 |
| (C–O) _{eq} | 1.143 | 1.152 |
| (ethylene)Fe(CO) ₄ (<i>C</i> _{2v}) (14) | | |
| Fe–CO _{ax} | 1.827 | 1.796(35) ^c |
| Fe–CO _{eq} | 1.807 | 1.836(35) |
| Fe–C1(C2) | 2.151 | 2.117(3) |
| C–H | 1.083 | 1.080 |
| C1–C2 | 1.462 | 1.46(6) |
| (1,3-butadiene)Fe(CO) ₃ (<i>C</i> _s) (15) | | |
| Fe–C4(C7) | 2.130 | 2.14 ± 0.04 ^d (2.086 ± 0.015) ^e |
| Fe–C5(C6) | 2.082 | 2.06 ± 0.03 (2.086 ± 0.015) |
| Fe–C2(C3) | 1.804 | 1.77 ± 0.03 (1.798 ± 0.015) |
| Fe–C1 | 1.793 | 1.74 ± 0.04 (1.798 ± 0.015) |
| C4–C5(C6–C7) | 1.421 | 1.46 ± 0.05 (1.410 ± 0.015) |
| C5–C6 | 1.413 | 1.45 ± 0.06 (1.410 ± 0.015) |
| (cyclobutadiene)Fe(CO) ₃ (<i>C</i> _s) (16) | | |
| Fe–C1(C4) | 2.073 | 2.063(10) ^f |
| Fe–C2(C3) | 2.044 | 2.051(4) |
| C1–C2(C4–C3) | 1.450 | |
| C1–C4 | 1.439 | 1.439(6) |
| C2–C3 | 1.463 | 1.456(15) |

^a B3LYP/6-311+G**. ^b Experimental values determined by gas-phase electron diffraction (ref 70). ^c Experimental values determined by gas-phase electron diffraction: Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, *21*, 401. ^d X-ray data (ref 73). ^e Gas-phase electron diffraction data (ref 74). ^f X-ray data (ref 75).

**Figure 6.** Calculated (GIAO/B3LYP/6-311+G**//B3LYP/6-311+G**) vs experimental ¹H chemical shifts for compounds **13–16**.

C_(ethylene) bond by 0.03 Å. Overall, however, this is a reasonable match between calculated and experimental geometries.⁷³

The structure of (butadiene)Fe(CO)₃ (**15**) has been determined by single crystal X-ray diffraction⁷⁴ and by gas-phase electron diffraction.⁷⁵ The overall computed structural features are in very good agreement with the experimental results (see Table 5). The carbon atoms of the diene unit are planar and the iron atom is about 1.64 Å from this plane. The Fe(CO)₃ group does not have local *C*_{3v} symmetry since one unique CO group is aligned with the open side of the diene while the other two are equivalent. The most common description of this coordination geometry is square pyramidal, with the iron atom lying above the basal plane defined by the two equivalent CO ligands and the midpoints of the outer C–C bonds of the diene.

**Figure 7.** Calculated (GIAO/B3LYP/6-311+G**//B3LYP/6-311+G**) vs experimental ¹³C chemical shifts (ppm) for compounds **13–16**.**Table 6.** Calculated Magnetic Susceptibilities for Compounds **13–16** (ppm cgs with sign reversed)

| compd | CSTG or IGAIM ^a | | | | |
|---|-----------------------------|----------------|----------------|------------------------------|-----------------|
| | ε ₁ ^b | ε ₂ | ε ₃ | χ _{av} ^c | Δχ ^d |
| Fe(CO) ₅ (13) | 65.13 | 65.09 | 65.01 | 65.09 | –0.11 |
| (ethylene)Fe(CO) ₄ (14) | 97.34 | 70.55 | 69.40 | 79.10 | –14.5 |
| (1,3-butadiene)Fe(CO) ₃ (15) | 105.9 | 95.00 | 68.81 | 89.91 | –31.6 |
| (cyclobutadiene)Fe(CO) ₃ (16) | 99.27 | 99.24 | 79.23 | 92.82 | –19.3 |

^a Both methods give the same values. ^b ε₁, ε₂, ε₃: eigenvalues of the magnetic susceptibility tensor as reported in the Gaussian 94 output file (where arbitrarily ε₁ < ε₂ < ε₃). ^c χ_{av} is the isotropic part [χ_{av} = 1/3(ε₁ + ε₂ + ε₃)]. ^d Δχ is the anisotropic part [Δχ = ε₃ – (ε₂ + ε₁)/2].

Finally, the calculated geometry of (cyclobutadiene)Fe(CO)₃ (**16**) in the staggered conformation is also in good agreement with the experimental results.⁷⁵ Low-temperature NMR studies show equivalent CO groups and equivalent ring positions⁷⁶ showing that there is a very low barrier to rotation of the iron tricarbonyl unit.

The proton and carbon chemical shifts calculated for **13–16** are presented as supporting information in Table 12 and compared with experimental data. Again the best agreement is given by the GIAO method. A graphical comparison of the calculated and experimental NMR data is shown in Figures 6 and 7, and the correlation is quite good.

The computed magnetic susceptibilities are shown in Table 6. The increments for χ_{av} based on the CSGT calculation (see Appendix) predict χ_{av}'[(localized cyclobutadiene)Fe(CO)₃] = –86.71 ppm cgs. Consequently the magnetic susceptibility exaltation for (cyclobutadiene)Fe(CO)₃ will be:

$$\begin{aligned} \Lambda[(\text{cyclobutadiene})\text{Fe}(\text{CO})_3] &= \\ \chi_{\text{av}}[(\text{cyclobutadiene})\text{Fe}(\text{CO})_3] - \\ \chi'_{\text{av}}[(\text{localized cyclobutadiene})\text{Fe}(\text{CO})_3] &= \\ -92.81 - (-86.71) &= -6.10 \text{ ppm cgs} \end{aligned}$$

which is negative and, although not a very large number, does correspond to an aromatic compound.

The magnetic susceptibility exaltation criterion for aromaticity is not a difficult result to obtain. When experimental magnetic susceptibility data for suitable model compounds are missing, they can now be easily and reliably calculated. The method needs no sensitive evaluation of the magnitude of accompanying effects, e.g. somewhat indeterminate strain energy considerations are a component of many homodesmotic energy criteria of

(73) Beagley, B.; Schmidling, D. *J. Mol. Struct.* **1974**, *22*, 466.(74) Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758.(75) Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, *21*, 401.(76) Nielsen, P. S.; Hansen, R. S.; Jakobsen, H. J. *J. Organomet. Chem.* **1976**, *114*, 145.

aromaticity. Because of these advantages, magnetic susceptibility exaltation has been shown to be an important experimental and/or theoretical test for the aromatic character of both organic and organometallic compounds. A recent theoretical extension of particular interest is the work of Schleyer et al.,³⁹ who have probed the aromatic character of the transition states occurring in some electrocyclic reactions.

Both calculation and experiment show the C–C bonds in an (arene)Cr(CO)₃ complex to have nearly equal bond lengths, indicative of complete electron delocalization,⁷⁷ a feature of both aromatic and antiaromatic systems. The latter terms are normally used to describe planar π -systems, and diamagnetic or paramagnetic ring currents (perpendicular magnetic susceptibility) are often attributed to such structures. In the present case, none of the previous NMR work (Introduction) would indicate a paramagnetic ring current in **1**, and we believe that the “antiaromaticity” calculated for **1** may also involve exalted in-plane susceptibility components.

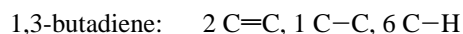
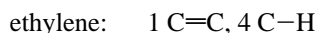
4. Conclusion

The hybrid HF-DFT (B3LYP/6-311+G**) level of ab initio MO theory provides excellent (relative to experimental quantities) equilibrium geometries, energies, frequencies, and magnetic properties for both organic and organometallic compounds, with comparable performance. This has allowed for the computation of the magnetic susceptibility exaltations (Λ) associated with both a purely organic system, benzene, and the complex of this with Cr(CO)₃ (organometallic). By this criterion, benzene is, as expected, aromatic and the Cr(CO)₃ complex antiaromatic. By way of comparison, a second organometallic compound, (cyclobutadiene)Fe(CO)₃, is calculated to be aromatic. We have also compared calculated ¹H and ¹³C anisotropic shielding parameters for benzene and (benzene)Cr(CO)₃ in order to evaluate in detail why the NMR chemical shifts for these are both located upfield in the complex.

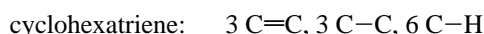
Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support.

Appendix. Derivation of the Theoretical Bond Increment System.

To get a bond increment system for benzene from calculations of ethylene (**7**) and the average of *s-trans*- (**8**) and *s-cis*-butadiene (**19**) (the protocol used in ref 12), we first note that these molecules consists of the following bonds:



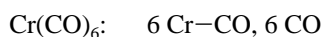
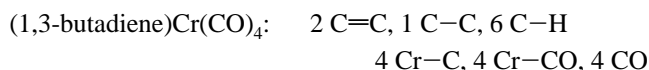
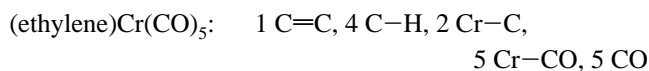
For a hypothetical polyene-like cyclohexatriene (or any isomer with three double bonds) we have:



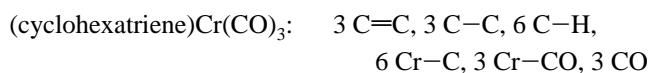
which corresponds to 3 times butadiene – 3 times ethylene.

(77) For the “group increment” equations listed in the Appendix, one can evaluate the homodesmotic energies. For benzene, $\Delta H^{298} = 33.2$ kcal/mol (using *cis*-butadiene), while for (benzene)Cr(CO)₃, a reduced value is obtained, $\Delta H^{298} = 19.9$ kcal/mol, in disagreement with the recent conclusion of Mitchell¹ that (benzene)Cr(CO)₃ is more “aromatic” (in the energy sense of this word) than benzene. However, the organometallic value is obtained as the difference of some large numbers and should be treated with some caution. This smaller but positive enthalpy for the organometallic homodesmotic equation implies a reduced delocalization energy compared to benzene but is obviously favorable compared to (cyclohexatriene)Cr(CO)₃, a result independently arrived at in the minimization of the (benzene)Cr(CO)₃ structure, where a (cyclohexatriene)Cr(CO)₃ structure would not have been excluded if it had indeed been the energy minimum.

In order to get an increment system that allows us a prediction for a hypothetical complexed cyclohexatriene from calculation of (ethylene)Cr(CO)₅ (**11**), (1,3-butadiene)Cr(CO)₄, (**12**) and Cr(CO)₆ (**10**), we first note that these molecules consist of the following bonds:

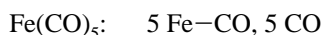
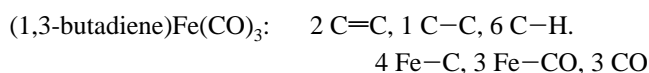
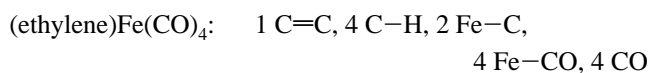


For a hypothetical complexed cyclohexatriene (or any isomer with three double bonds) we have:

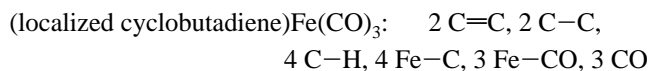


which corresponds to 3 times (1,3-butadiene)Cr(CO)₄ – 3 times (ethylene)Cr(CO)₅ + Cr(CO)₆.

In order to get an increment system that allows us a prediction for a hypothetical complexed localized cyclobutadiene from calculation of (ethylene)Fe(CO)₄ (**14**), (1,3-butadiene)Fe(CO)₃ (**15**), and Fe(CO)₅ (**13**), we first note that these molecules consist of the following bonds:



For a hypothetical complexed localized cyclobutadiene we have:



which corresponds to 2 times (1,3-butadiene)Fe(CO)₃ – 2 times (ethylene)Fe(CO)₄ + Fe(CO)₅.

Supporting Information Available: Table 7, calculated (B3LYP/6-311G**) geometrical parameters for **11** and **12**; Table 8, total energies (au), together with the ZPVE (kcal/mol) and thermal corrections (kcal/mol) for **1**, **2**, and **7–16**; Tables 9 and 10, calculated (B3LYP/6-311+G**//B3LYP/6-311+G**) harmonic and observed fundamental frequencies (in cm⁻¹) for **10** and **1**; a plot of uncorrected calculated values vs experimental ones for **10** (Figure 8); Tables 11 and 12, computed (GIAO, CSGT, IGAIM//B3LYP/6-311+G**//B3LYP/6-311+G**) and experimental chemical shifts (δ) (ppm) for compounds **1**, **2**, **7–12**, and **13–16** (9 pages). See any current masthead page for ordering and Internet access instructions.