Does $Cr(CO)_3$ Complexation Reduce the Aromaticity of Benzene?

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Received June 23, 1999

Abstract: Ring currents in $(C_6H_6)Cr(CO)_3$, **1**, (*cis*-1,3-butadiene)$Cr(CO)_4$ (**4**), $(C_6H_6)_2Cr$ (**5**), $(C_4H_4)Fe(CO)_3$ (**6**), and (*cis*-1,3-butadiene)$Fe(CO)_3$ (**8**) have been assessed by $\sigma-\pi$ disected nucleus independent chemical shift (NICS) calculations. Shielding contributions from the C−C(π) orbitals to the NICS values reveal that there is no quenching of ring current in the benzene ring of **1** or in dibenzene chromium **5**. The previously reported paratropic ring current for **1** is shown to be a consequence of latent aromaticity in 1,3-butadiene chromium tetracarbonyl **4** (one of the molecules used in the magnetic susceptibility equation). NICS values, a diatropic ring current, and a positive aromatic stabilization energy (ASE) all point to this aromaticity. NICS values for cyclobutadiene iron tricarbonyl, **6**, show moderately sized diamagnetic shielding above the plane of the four-membered ring. In addition, **6** has a negative magnetic susceptibility exaltation (MSE) (diatropic ring current), quite opposite from the large paratropic current calculated for cyclobutadiene (D_{2h}) itself. Evaluated using "strain corrected" isodesmic reactions, **6** has a large ASE in contrast to a large destabilization calculated for cyclobutadiene with the same equation. The 1,3-butadiene complex **8** also shows features of three-dimensional aromaticity, NICS(1) −8.7, $NICS(1)_\pi$ −2.8, and a moderate ASE stabilization energy (7.9 kcal/mol, eq 7), but this complex has a negligible MSE of −1.0 ppm cgs. We predict the ring current order to be the following: benzene ∼ **1** ∼ **5** > **6** > **4** > **8**.

Introduction

The effect of $Cr(CO)_3$ complexation on the aromaticity of benzene has been debated for over 30 years.[1−11] Such complexation results in a 2 ppm shift of the benzene protons in $(C_6H_6)Cr(CO)_3$ (**1**), i.e., into the olefinic region, but reduction of the ring current is only one of the possible reasons.[2−11] Cleverly designed molecules (e.g. **2** and **3**) in which monitor protons are located above arene ring faces, presumably in the shielding zones, gave conflicting results. Keller reported[3] only small (0.05 ppm) additional shielding on complexation to form **2** but the proton is 2.628 Å from the ring.[12] The two rings in metacyclophane, **3**, afforded a direct comparison.[9] The monitor proton involved with the complexed arene was 1.3 ppm downfield of the signal for its counterpart indicating a weakening of the ring current due to $Cr(CO)_3$ complexation. Again these monitor protons are rather remote (2.635 Å for **3**)[12] and are not located in the optimum positions, i.e., directly above the ring centers (cf. **2** and **3**). No definite answer to the title question can be deduced from these studies.The two most recent investigations employed quite different methods and came to opposite conclusions.[1,2] The changes in geometry (reduced bond fixations), as observed from the NMR chemical shifts, in a $Cr(CO)_3$ complex of benzoannulated-[14]annulene were interpreted to show that complexation actually increased the aromaticity of the benzene moiety.[2]

Simion and Sorensen[1] evaluated the magnetic susceptibility exaltation (MSE)[13−15] of **1**, as well as the aromatic stabilization energy (ASE) by employing isodesmic eq 1 (computed at the B3LYP/6-311+G** levels). The comparison data for the similar evaluation of benzene (eq 2) indicates that **1** is antiaromatic (positive MSE) and has sharply reduced ASE.

$$\mathbf{1}\ (C_{3v}) + 3(\text{ethylene})\text{Cr(CO)}_5\ (C_{2v}) = 3(\text{1,3-butadiene})\text{Cr(CO)}_4\ (C_s) + \text{Cr(CO)}_6\ (O_h) \quad (1)$$

$$\text{MSE}(\Lambda) = 12.3\ \text{ppm cgs};\ \text{ASE}(\Delta E) = 18.5\ \text{kcal/mol}$$

$$C_6H_6\ (D_{6h}) + 3C_2H_4\ (D_{2h}) = 3C_4H_6\ (C_{2v}) \quad (2)$$

$$\text{MSE}(\Lambda) = -15.1\ \text{ppm cgs};\ \text{ASE}(\Delta E) = 34.1\ \text{kcal/mol}$$

We now propose a resolution to these seeming discrepancies. We apply a refined NICS (Nucleus Independent Chemical Shift) method, which gives the individual contributions to the NICS

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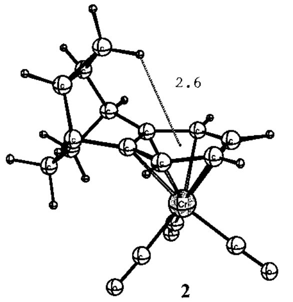
10.1021/ja9921423 CCC: \$19.00

Chart 1



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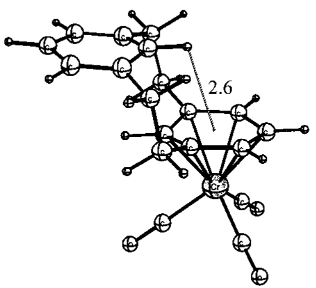

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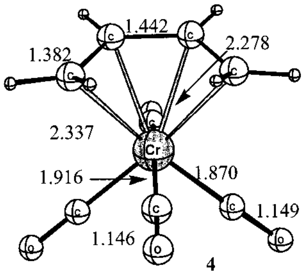

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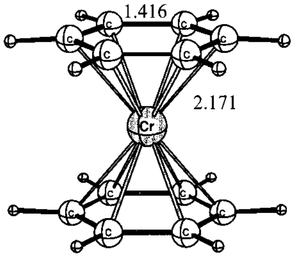

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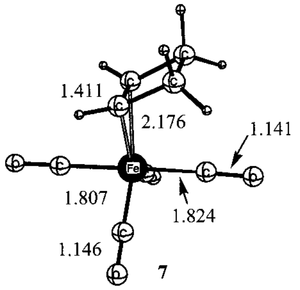

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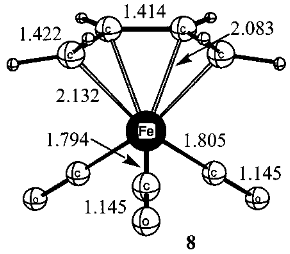

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shielding from the metal, C−C(σ), C−C(π), C−H, M−C, etc., localized orbitals[16−20] to analyze the ring currents in **1**, (*cis*-1,3-butadiene)Cr(CO)$_4$ (**4**), $(C_6H_6)_2Cr$ (**5**), $(C_4H_4)Fe(CO)_3$ (**6**), and (*cis*-1,3-butadiene)Fe(CO)$_3$ (**8**). The total C−C(π) contribution (NICS$_\pi$) is a particularly relevant measure of aromaticity.

Calculation Methods

Structures **1**, **4**, **5**, **6**, **7**, **8**, ethene (D_{2h}), *cis*-1,3-butadiene (C_{2v}), cyclobutane (D_{2d}), cyclobutene (C_{2v}), cyclobutadiene (D_{2h}), benzene (D_{6h}), Cr(CO)$_6$ (O_h), and Fe(CO)$_5$ (D_{3h}) were optimized at the B3LYP/6-311+G** level, either taken from ref 1 or carried out in the present study, using the Gaussian 94 program.[18] Magnetic susceptibilities were obtained at the same level using the CSGT procedure. NICS calculations were carried out at the SOS-DFT-IGLO level[19a,b] using the Perdew-Wang-91 exchange correlation functional and the IGLO III TZ2P basis set with the Pipek-Mezey localization procedure[19c] as implemented in the deMon NMR program.

Results and Discussion

NICS values were obtained at a central point in the plane of the rings (NICS(0)), or at points above the ring, e.g. NICS(1) refers to calculations at a distance of 1.0 Å above the ring. NICS values can also be dissected into the contributions from various bonds in the molecule. Large negative NICS$_\pi$ values indicate a diatropic ring current (NMR shielding).

The NICS(0) and NICS(1) values for **1** and for benzene are shown in Table 1. The large NICS(0) value for **1**, −25.8, as compared to benzene (−8.8), can be understood from the dissected NICS calculations (Figure 1). The paratropic contributions from the C−C(σ) bonds of the benzene ring in **1** at NICS(0) (11.9) and for free benzene (13.8) are very similar. For both **1** and benzene, the major contribution to the NICS(0) comes from the C−C(π) orbitals of the benzene ring, NICS(0)$_\pi$ −23.2 for **1** and −20.7 for benzene (Table 1), indicating strong aromaticity. At 1.0 Å above the ring plane the contributions from the C−C(σ) bonds (2.8) and from the metal (−3.2) for **1** are much reduced but the C−C(π) contributions (−9.3) are substantial. Similar results can be seen for benzene, NICS(1)$_\sigma$ (2.4), and NICS(1)$_\pi$ (−9.6).

If **1** exhibits as strong a ring current as that of benzene, why did the MSE evaluation using eq 1 result in positive values? Isodesmic equations such as eqs 1 and 2 are valid only if the reference compounds have no ring current effects, which is true for eq 2 but not for eq 1. The butadiene complex, **4**, is a three-dimensional aromatic compound[21] and has exalted magnetic susceptibilities (eq 3). Since eq 1 employs three butadiene complexes (**4**) for each benzene ring in **1**, the “3 vs 1” weighting results in a bias.

$$\mathbf{4}\ (C_s) + \mathrm{Cr(CO)_6}\ (O_h) + 2\mathrm{C_2H_4}\ (D_{2h}) = \mathrm{C_4H_6}\ (C_{2v}) + 2(\mathrm{ethylene})\mathrm{Cr(CO)_5}\ (C_{2v}) \quad (3)$$

$$\mathrm{MSE}(\Lambda) = -9.7\ \text{ppm cgs};\ \mathrm{ASE}(\Delta E) = 6.3\ \text{kcal/mol}$$

After correcting eq 1 for the exaltation of $(C_4H_6)Cr(CO)_4$, the MSE (−17.2 ppm cgs) and ASE (37.5 kcal/mol) of **1** (eq 4) are similar to the benzene values (eq 2).

$$\mathbf{1}\ (C_{3v}) + 2\mathrm{Cr(CO)_6}\ (O_h) + 6\mathrm{C_2H_4}\ (D_{2h}) = 3\mathrm{C_4H_6}\ (C_{2v}) + 3(\mathrm{ethylene})\mathrm{Cr(CO)_5}\ (C_{2v}) \quad (4)$$

$$\mathrm{MSE}(\Lambda) = -17.2\ \text{ppm cgs};\ \mathrm{ASE}(\Delta E) = 37.5\ \text{kcal/mol}$$

The benzene ^{1}H chemical shifts in **1** (5.8) and in free benzene (7.6) differ by 1.8 ppm (Table 1). The difference in the ^{1}H chemical shifts of **1** and benzene is due to the changes in the electron density of the C−H bonds, as the shielding contributions of C−C(π) orbitals for **1** (2.1) and for benzene (2.2) are very similar.[22,23] Judging from the NICS(1)$_\pi$, MSE, and ASE values, there is no disruption of the ring current of benzene on complexation.

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(20) The total NICS value at the center of an aromatic compound (and above) is a sum of paratropic contributions (mostly from C−C(σ) bonds) and diatropic contributions (notably C−C(π) bonds) (Table 1). The paratropic contributions fall off quickly above the ring plane compared to the diatropic values.

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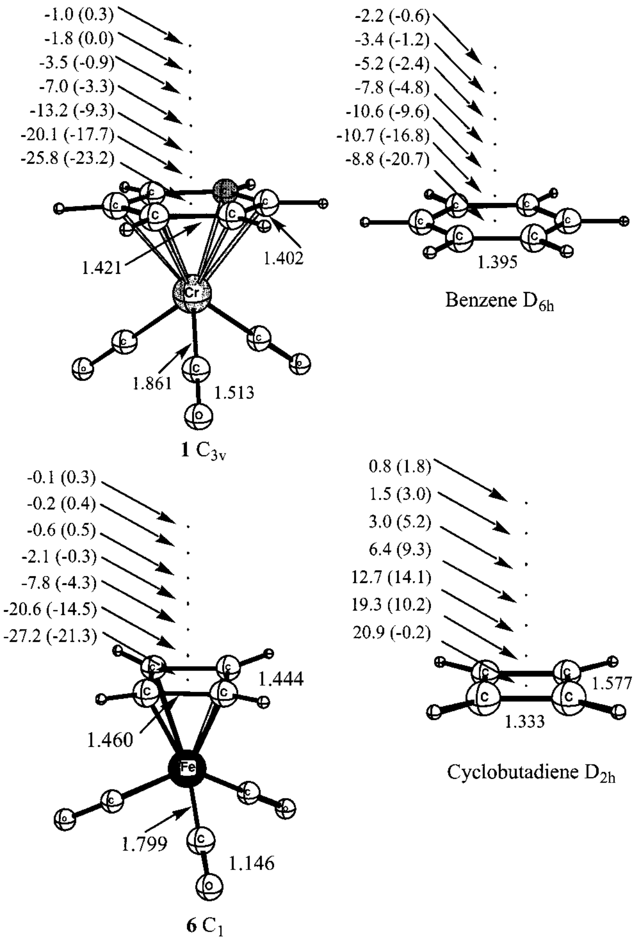
Table 1. The C−C and Metal−Carbon (M−C) Bond Lengths, NMR Shielding Contributions (signs reversed) from the Various Localized MO's to the Total Nucleus Independent Chemical Shift (NICS) Values at IGLO/III//B3LYP/6-311+G**, along with the Proton Chemical Shifts

	C−C(Å)	M−C(Å)^a	NICS	NICS$_\sigma$	NICS$_\pi$	C−H	M−C^a	rest^c	^{1}H(C−H)
benzene (D_{6h})	1.395		−8.8(−10.6)^b	13.8(2.4)	−20.7(−9.6)	−1.3(−2.0)		−0.6(−1.4)	7.6(−1.2)^d
cis−1,3-butadiene (C_{2v})	1.337, 1.470		0.3(−1.1)	6.7(0.9)	−6.4(−0.6)	0.2(0.0)		−0.5(0.0)	5.8(−1.4)
C_4H_4 (D_{2h})	1.333, 1.577		20.9(12.7)	22.2(1.7)	−0.2(14.1)	−1.6(−2.8)		−0.5(−0.3)	5.9(−1.0)
1 (C_{3v})	1.421, 1.402	2.247	−25.8(−13.2)	11.9(2.8)	−23.2(−9.3)	−4.1(−3.9)	−8.3(−3.2)	−2.1(0.0)	5.8(−0.3)
4 (C_s)	1.383, 1.442	2.374, 2.227	−16.3(−6.9)	3.4(2.6)	−9.2(−4.2)	−2.7(−2.4)	−8.1(−3.3)	0.3(0.4)	3.7(−0.2)
5 (D_{6h})	1.416	2.171	−37.8(−17.4)	9.2(3.0)	−21.9(−9.3)	−3.0(−3.0)	−10.4(−4.0)	−11.5(−4.1)	4.5(−0.4)
6 (C_1)^e	1.442, 1.444	2.08, 2.06	−30.1(−7.7)	11.4(3.1)	−21.4(−4.3)	−6.1(−4.2)	−10.1(−2.4)	−3.9(−0.9)	2.5(−0.2)
	1.459, 1.460	2.06, 2.04							
8 (C_s)	1.421, 1.413	2.130, 2.082	−19.8(−8.7)	3.1(2.3)	−6.4(−2.8)	−3.2(−2.1)	−13.8(−6.0)	0.4(−0.1)	4.3(0.7)

^{a} M−C, metal−carbon distances. ^{b} NICS(1) values are given in parentheses. ^{c} Contributions from the core AO's, lone pairs, and valance AO's of transition metals. ^{d} ^{1}H chemical shifts relative to TMS; relative (TMS) chemical shifts of C−H bond contributions are given in parentheses. ^{e} In ref 1, the structure of **6** was calculated in a C_s symmetry such that one CO group bisects the C−C bonds of the cyclobutadiene unit. However, an X-ray structure shows the other C_s geometry: Harvey, P. D.; Schaefer, W. P.; Gray, H. B.; Gilson, D. F. R.; Butler, I. S. *Inorg. Chem.* **1988**, *27*, 57. Optimization of **6** in C_1 symmetry gives a structure very close to the X-ray geometry but with the same energy as for the previous calculation, showing that the Fe(CO)$_3$ is nearly a free rotor. The magnetic susceptibility is identical for both calculated geometries. We thank W. Herndon for informing us of this discrepancy and of his own calculations of this system.



1 C_{3v}

Benzene D_{6h}

6 C_1

Cyclobutadiene D_{2h}

Figure 1. Total NICS values of **1** and benzene (IGLO/III/B3LYP/6-311+G**) calculated at the center of the six-membered rings and at points 0.5 Å apart. The C−C(π) contributions to NICS are given in parentheses.

Replacement of the three carbonyl groups in **1** by another benzene, $(C_6H_6)_2Cr$ (**5**), shortens the M−C$_{ring}$ distances in **5** (2.171 Å) compared to **1** (2.247 Å) and results in equal C−C bond lengths. While the total NICS(0) (−37.8) and NICS(1) (−17.4) values of **5** are even larger than **1** (Table 1), the C−C(π) contributions to NICS are very similar (NICS(0)$_\pi$ −21.9 and NICS(1)$_\pi$ −9.3 for **5** and −23.2 and −9.3 for **1**) (Table 1). The changes in metal contributions influence the total NICS values but have negligible effects on the ring current.

In contrast to the negative NICS values, downfield ^{1}H chemical shifts, and diatropic contributions from the π electrons of benzene, singlet cyclobutadiene (D_{2h}) displays the opposite behavior (positive NICS values, no change in the chemical shifts of protons and paratropic contributions from π electrons) (Table 1).[24] A widely recognized example of a metalloaromatic complex is $(C_4H_4)Fe(CO)_3$, **6**.[25] The behavior of $(C_4H_4)Fe(CO)_3$, **6**, and cyclobutadiene also is completely different. Most significant are the NICS(1) (−7.7 for **6** and 12.7 for C_4H_4 (D_{2h})) and NICS(1)$_\pi$ (−4.3 for **6** and 14.1 for C_4H_4 (D_{2h})) values. Likewise, using the "strain corrected" eqs 5 and 6, the paratropic MSE for C_4H_4 (D_{2h}) is reversed, and the ASE becomes highly stabilizing for Fe(CO)$_3$ complexation, befitting the aromatic character of **6**.

$$\mathbf{6}\ (C_1) + \text{cyclobutane}\ (D_{2d}) + \text{Fe(CO)}_5 = 2(\text{cyclobutene})\text{Fe(CO)}_4\ (C_1)\ \mathbf{7} \quad (5)$$

$$\text{MSE}(\Lambda) = -19.8\ \text{ppm cgs};\ \text{ASE}(\Delta E) = +24.1$$

$$C_4H_4\ (D_{2h}) + \text{cyclobutane}\ (D_{2d}) = 2\text{cyclobutene}\ (C_{2v}) \quad (6)$$

$$\text{MSE}(\Lambda) = +9.8\ \text{ppm cgs};\ \text{ASE}(\Delta E) = -35.4$$

The eq 5 ASE value is a very realistic estimate of the aromaticity associated with **6** since an attempt is made to account for the strain energy of the four-membered ring in **6**. The eq 6 ASE is also "strain corrected" and the total 59.5 kcal/mol difference in the two energies is a measure of how much cyclobutadiene is stabilized by the Fe(CO)$_3$ complexation.

Do the NICS values for the 1,3-butadiene complexes, (C_4H_6)-Cr(CO)$_4$, **4**, and $(C_4H_6)Fe(CO)_3$, **8**, provide evidence for three-dimensional aromaticity?[21] In agreement with the −9.7 ppm cgs MSE and 6.3 ASE for **4** (eq 3), the NICS(1) −6.9 and NICS(1)$_\pi$ −4.2 are significant compared to the corresponding values NICS(1) −1.1 and NICS(1)$_\pi$ −0.6 for *cis*-1,3-butadiene (C_{2v}). The $(C_4H_6)Fe(CO)_3$, **8**, has NICS(1) −8.7 and NICS(1)$_\pi$ −2.8 but a negligible MSE −1.0 ppm cgs and moderate stabilization

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(22) The shielding contributions of **1** and benzene are (signs not reversed) as follows: for **1** total 25.2; individual MO contributions C−H (24.6), rest of the C−H (−0.1), C−C(σ) (−2.6), C−C(π) (2.1), C−O (−0.5), Cr−C (1.2), and Core (0.5); for benzene: total 23.7; C−H (25.7), rest of the C−H (−0.2), C−C(σ) (−3.7), C−C(π) (2.2), and Core (−0.3).

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ASE (7.9 kcal/mol) (eq 7). On the basis of the magnetic properties, **8** seems to be less aromatic than **4**.

$$\mathbf{8}\ (C_s) + \mathrm{Fe(CO)_5}\ (D_{3h}) + 2\mathrm{C_2H_4}\ (D_{2h}) = 2\mathrm{(ethylene)Fe(CO)_4}\ (C_{2v}) + \mathrm{C_4H_6}\ (C_{2v}) \quad (7)$$

$$\mathrm{MSE}(\Lambda) = -1.0\ \mathrm{ppm\ cgs};\ \mathrm{ASE}(\Delta E) = 7.9\ \mathrm{kcal/mol}$$

We conclude that $Cr(CO)_3$ complexation does not reduce the aromaticity of benzene, judging from the $\mathrm{NICS}(1)_\pi$ values of benzenes in **1** and **5** to that of benzene itself. In contrast, the strongly antiaromatic cyclobutadiene becomes aromatic in the $Fe(CO)_3$ complex, and the latter shows a large diatropic ring current. The three-dimensional aromaticity of the butadiene complex of $Cr(CO)_4$, **4**, is larger than that of the $Fe(CO)_3$ complex, **7**. Based on the C−C(π) contributions to the NICS at 1.0 Å ($\mathrm{NICS}(1)_\pi$) the ring current order is the following: benzene ∼ **1** ∼ **5** > **6** > **4** > **8**.

Acknowledgment. P.v.R.S. and B.K. thank the Deutsche Forschungsgemeinschaft for financial support. D.V.S. and T.S.S. thank the Natural Sciences and Engineering Research Council of Canada for a scholarship and other financial support.

JA9921423