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The Competition for Electrons: Aromatic Stabilization in a Six-Membered Ring vs Cyclobutadiene−Iron Complex. The Molecular Structure of Tris(tricarbonylironcyclobutadieno)benzene

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The title compound was prepared from hexabromotricyclobutabenzene and diiron nonacarbonyl, and its X-ray structure was measured. The C−C bonds in the six-membered ring are longer than in an typical aromatic moiety (1.443−1.470 Å), suggesting that the system is best regarded as three C(sp^2)−C(sp^2) single bonds connecting three $(CO)_3Fe$−cyclobutadiene complexes. It is shown that the effect of complexing tricarbonyliron to a benzocyclobutadiene moiety is not additive. Ab initio calculations and NRT analyses were used to understand the geometrical, electronic, and energetic properties of the systems. It was found that complexation of $(CO)_3Fe$ to benzocyclobutadiene aromatizes the systems, whereas the opposite is happening upon complexation of three iron moieties to tris(cyclobutadieno)benzene. The study of the energy required for the deformation of the ligands to their geometry in the complex suggests that the iron−cyclobutadiene bond is stronger in the title complex than in $(CO)_3Fe$−cyclobutadiene. The title complex shows a small but significant Mills−Nixon effect.

Introduction

The issue of aromaticity was thought to be understood since Hückel presented his work in the area, but about 15 years ago Shaik et al. challenged this perception, claiming that the special structural and chemical properties of aromatic systems (e.g., benzene) are an outcome of the σ frame, and the π system is more stable when localized.[2] The subject is heavily debated since,[3] but to the best of our knowledge, quantitative experimental answers are not available as yet. Nevertheless, the term "aromatic stabilization" is still well accepted, and is estimated to be 36 kcal mol^{-1} for benzene.[3a,4]

This issue could be rephrased as the relative importance of π vs σ frames in aromatic systems. Which of the two actually controls the properties of the systems? The fact that "aromatic stabilization" (of a cyclic $4n + 2$ electron system) is a good working hypothesis that explains many reactions, transition-state-stabilization and energetics does not necessarily prove that the π system actually controls these properties. It may well be that the σ frame imposes some structural and/or electronic features, and, within these constraints, the π system, minimizing its energy, obtains its properties. To separate between these two, one needs a property that will distinguish between the π and the σ frames, i.e., a property that will affect primarily one of these systems and allow the study of the characteristics of the molecule. Such tools may be transition metal fragments bound to the aromatic moiety and/or strain imposed on the σ frame (the Mills−Nixon effect[5]).

Binding a metal atom or fragment to a π system clearly weakens the π bond, as it involves shifting bonding electron density from the bonding orbitals of the ligand to the metal (bonding) and pushing electron density from the metal to the antibonding π^* orbitals of the ligand (back-bonding). The geometrical effects of binding a metal to a π ligand are lengthening of the bonds and pyramidalization of the attached atoms. While changing the chemical properties of the π ligand,[6] it is accepted that arene−metal complexes are less aromatic than are the free arenes, although there is some evidence that it is not always so.[7] On the other hand, the antiaromatic cyclobutadiene is unknown as a free ligand (unless heavily substituted)[8] but is stable as an organometallic

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[1] (a) Haifa. (b) Essen.

[2] (a) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (b) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (c) Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908. (d) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (e) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Chem. Phys* **1988**, *92*, 5086.

[3] (a) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. (b) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132, and references therein, especially (c) Jug, K.; Köster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772. (d) Glendening, E. D.; Faust, R.; Streitwieser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952. (e) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048. (f) Jenneskens, L. W.; van Eenige, E. N.; Vlietstra, E. J. *New J. Chem.* **1994**, *18*, 553. (g) Ichikawa, H.; Kagawa, H. *J. Chem. Phys.* **1995**, *99*, 2307. (h) See ref 2.

[4] See for example: Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan Publishing Company: New York, 1992; pp 604−611.

[5] Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.

[6] For example, the benzene in $(CO)_3Cr(C_6H_6)$ is susceptible to nucleophilic attacks.

[7] Mitchell, R. H.; Zhou, P.; Venugopalan, S.; Dingle, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 7812.

[8] Although heavily substituted cyclobutadiene is known (e.g., tetra-*tert*-butyl) the system cannot be considered as antiaromatic (it is nonaromatic) as it is rectangular and not symmetric. See Dunitz, J. D.; Krüger, C.; Irngartinger, H.; Maverick, E. F.; Wang, Y.; Nixdorf, M. *Angew. Chem.* **1988**, *100*, 415. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 387, and references therein.

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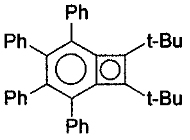
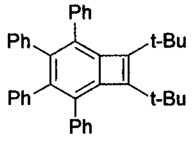
complex.[9] It can be thus concluded that binding transition metal to the π system of an aromatic or antiaromatic system perturbs the σ system only to a small degree (if at all) and thus could serve as a probe for the study of the σ vs π importance in aromatic systems.

Strain in the Mills–Nixon-effect manner[5] affects primarily the σ system, as it acts in a plane that is orthogonal to the π system. Lately, it has been shown that strain indeed localizes aromatic systems.[10] Thus, the study of the Mills–Nixon effect can principally serve as a complimentary (to transition metal π complexes) tool for the issue discussed above.

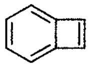
Benzocyclobutadiene contains potential aromatic and antiaromatic moieties that are mutually dependent.[11] In addition, it contains strain that may impose bond localization.[10] Experimentally, the structure of **1** is known,[12] suggesting that the dominant resonance structure is **1a**. The tricarbonyliron complex of **1** is also known (**2**)[13] and shows less localization than the free ligand and to the other direction (e.g., "anti-Mills–Nixon" structure). However, due to the heavy substitution it is unclear which factors (i.e., electronic, strain, or steric congestion) govern the structures of **1** and **2**. The parent benzocyclobutadiene **3** is unstable and therefore experimentally unknown, but its tricarbonyliron complex (**4**) has been prepared[14] and structurally characterized.[15] Its basic geometrical features are similar to those of **2** but not quantitatively.



1



1a



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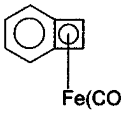
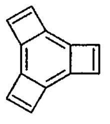
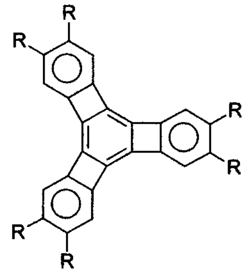


4

In tris(cyclobutadieno)benzene **5** the strain and aromaticity factors are even more pronounced than in **3**. Experimentally, a tribenzo derivative is known (**6**),[16] and the system shows pronounced bond localization.



5



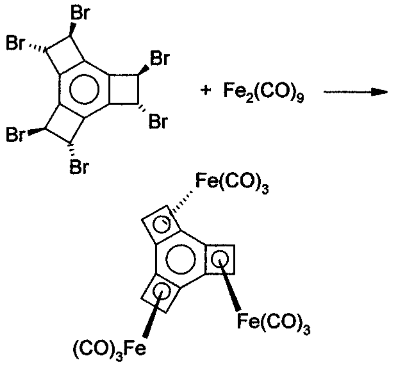
6 **R=TMS, H**

The questions we address here are what happens when **5** is forced to have its four-membered rings as cyclobutadienes by complexing tricarbonyliron to each of them. Will the system be localized (as is the free ligand) or show reversed localization as does **3**? Will aromaticity–antiaromaticity forces play a role in determining the structural properties of the system? What will be the effect (if any) of strain on the structure? In the competition for the π electrons between the benzene system (i.e., benzene's aromaticity) and cyclobutadiene ligands,[9] which is stronger? Could this system give an answer about the σ and the π interplay in aromatic systems? And finally, what is the role of $Fe(CO)_3$ on the structure and electronic properties; would the change in geometry of the ligand (e.g., tris(cyclobutadieno)benzene) be enough to account for the electronic changes, or does the actual binding make the changes?

To answer these questions we have studied the geometries of **3** and **5** using ab initio methods, so that the geometries of the free ligands could be obtained with reasonable accuracy and the interactions analyzed quantitatively. We have prepared and characterized **7** and compared its structure with the geometry of the free ligand. The results are reported here.

Results and Discussion

(i) The Preparation and Structure Determination of 7. The compound was prepared (in 20% yield) by reacting hexabromotricyclobutabenzene[17] with diiron nonacarbonyl in pentane at room temperature (eq 1). Only **7a** is obtained (as evident from the ^{1}H and ^{13}C NMR spectra),[18] probably due to steric congestion in **7b**. Crystals suitable for X-ray structure determination were



(1)

7

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(9) Cyclobutadiene–$Fe(CO)_3$ is considered to be aromatic (e.g., possess aromatic stabilization) in contrast to the nonaromatic free ligand. See: (a) Aihara, J.-I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1541. (b) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. (c) Herndon, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 1538. (d) Harvey, P. D.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chem.* **1986**, *25*, 1009.

(10) (a) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721. (b) Frank, N. L.; Siegel, J. S. In *Advances in Theoretically Interesting Molecules*; JAI Press Inc.: Greenwich, CT, 1995; Vol. 3, pp 209–260. It is also understood why apparently strained systems (like, for example, tricyclobutabenzene) do not show large bond fixation. See (c) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.

(11) If the six-membered ring is delocalized, the four-membered ring becomes antiaromatic or nonaromatic, which implies a considerable lengthening of the two "single" bonds.

(12) (a) Winter, W.; Straub, H. *Angew. Chem.* **1978**, *90*, 142. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 127. (b) Winter, W.; Butters, T. *Acta Crystallogr.* **1981**, *B37*, 1524.

(13) Winter, W.; Butters, T. *Acta Crystallogr.* **1981**, *B37*, 1528.

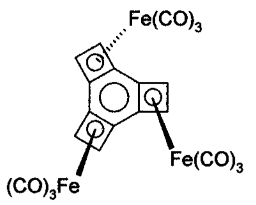
(14) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131.

(15) Stanger, A.; Ashkenazi, N.; Boese, R.; Stellberg, P. *J. Organomet. Chem.* **1997**, *542*, 19.

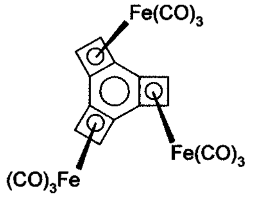
(16) (a) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150. (b) Boese, R.; Vollhardt, K. P. C., unpublished results.

(17) Stanger, A.; Ashkenazi, N.; Boese, R.; Bläser, D.; Stellberg, P. *Chem. Eur. J.* **1997**, *3*, 208.

(18) For **7b** one proton and three carbon resonances are expected. For **7a**, due to its reduced symmetry, more signals are expected (see Experimental Section).



7a



7b

obtained by slow crystallization from hexane solution at −20 °C. The crystal structure (Figure 1)[19] confirms the NMR based assignment of the relative arrangement between the Fe(CO)$_3$ moieties, i.e., two at the same side and one at the opposite side of the ligand. The tris(cyclobutadieno)benzene ligand deviates from planarity quite considerably; the four-membered rings form angles of 12.8 (the ring bound to the anti Fe(CO)$_3$), 19.2, and 20.2° with the six-membered ring that is essentially planar. The average bond length of the six-membered-ring bonds exocyclic to the four-membered rings is 1.443(7) Å, whereas the average endocyclic bond length is 1.468(7) Å. Thus, a small but significant Mills−Nixon localization is found, corresponding to an effective bond angle of 112.0°,[10] whereas the measured bond angle is 89.3(2)°, i.e., a considerable curvature of the bonds is expected. This is in contrast to the situation in **4**, where an "anti-Mills−Nixon" geometry is found.[15] Another interesting feature in the structure is the long bond lengths observed, which suggests that the six-membered ring bonds in **7** are of a considerable single-bond character. Below we discuss the effect of the nonplanarity of the system and the general geometrical features of **7**.

(ii) Geometries of the Free Ligands. Ab initio calculations[20] were used in order to access the geometries of benzocyclobutadiene (**3**) and tris(cyclobutadieno)benzene (**5**). A complete (within the limitations of the program and the computer) study was carried out on **3**, and the results are presented in Table 1. From these results it is clear that the limit of description of the geometry at Hartree−Fock level is obtained at 6-31G* basis set, as the geometry does not change significantly with the addition of another valence function and polarization on the hydrogen atoms, i.e., 6-311G**. However, addition of CI (at MP2 level) changes considerably the optimized geometry. DFT procedure (at B3-LYP/6-31G* level) yields results that can be regarded best, because most of the geometrical parameters (except R$_1$ and R$_5$ which do not change significantly at all the levels of theory where 6-31G* basis set was employed) fall between HF/6-31G* and MP2/6-31G*; the latter has the tendency to overshoot the effect of correlation. These observations are in accordance with the findings of Siegel

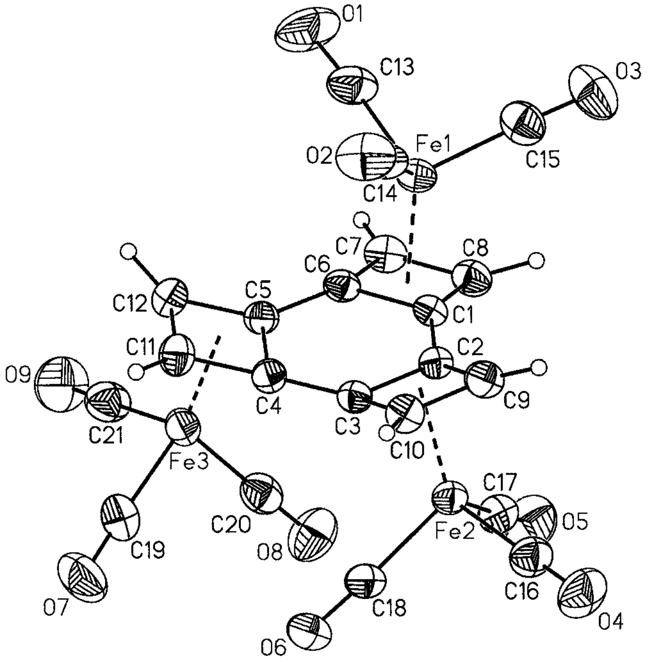
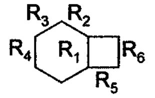


Figure 1. 30% Ellipsoid plot of **7a**. Relevant distances (Å) and angles (deg): C(1)−C(2) 1.449(6); C(2)−C(3) 1.456(6); C(3)−C(4) 1.429(6); C(4)−C(5) 1.469(6); C(5)−C(6) 1.451(6); C(6)−C(1) 1.480(5); C(six-membered ring)−C(four-membered ring), mean value, 1.440(6); Outer C−C bonds, mean value, 1.425(9). Mean angle for the fused bonds (e.g., C(8)−C(1)−C(6)) 89.3(3). Mean angle for the six-membered ring (e.g., C(1)−C(2)−C(3)) 120.0(4). Mean angle for the external four-membered rings (e.g., C(1)−C(8)−C(7)) 90.7(3).

Table 1. Geometrical Parameters of Benzocyclobutadiene at Different Theoretical Levels



	HF/ 3-21G	HF/ 6-31G*	HF/ 6-311G**	MP2/ 6-31G*	B3-LYP/ 6-31G*
R$_1$	1.4258	1.4221	1.4220	1.4200	1.4247
R$_2$	1.3395	1.3416	1.3404	1.3676	1.3614
R$_3$	1.4375	1.4398	1.4402	1.4284	1.4368
R$_4$	1.3584	1.3576	1.3561	1.3864	1.3785
R$_5$	1.5460	1.5174	1.5178	1.5212	1.5245
R$_6$	1.3365	1.3327	1.3328	1.3595	1.3518

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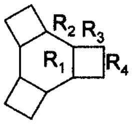
(19) Crystallographic data of **7a**. An orange crystal of $C_{21}H_6Fe_3O_9$ with the approximate dimensions of 0.22 × 0.17 × 0.11 mm^3 was measured on a Siemens SMART CCD area detector system with three axis geometry with Mo Kα radiation at 298 K. Crystal data and refinement details: Crystal system monoclinic; cell dimensions a = 7.5216(2), b = 18.7945(3), c = 14.8483(4) Å, β = 93.4021(9)°, V = 2095.33(9) Å^3 (refined from 5896 reflections), $Z = 4$, $\rho_{calcd} = 1.806$ mg/m^3, $\mu = 2.101$ mm^{-1}, space group $P2_1/c$, full sphere data collection in ω at 0.3° scan width in four runs with 606, 435, 606, and 435 frames (ϕ = 0, 88, 180, and 270°) at a detector distance of 5.891 cm ($2\Theta_{max}$ = 46.5°), data reduction with SAINT program (V4.050, Siemens) by which more than 98% of the data are covered, decay correction (<2%) by repeated collection of 50 frames at the end of the data collection, empirical absorption correction with redundant data (SADABS program, Siemens) max/min transmission 1.00/0.74, R(merg) before/after correction 0.0583/0.0391. 13216 intensities processed, 3001 unique and 2270 observed [$F_o > 4\sigma(F)$] (R_{int} = 0.0390). Structure solution and refinement on F^2 with SHELXTL-Plus Ver. 5.03/Iris (Siemens), 298 parameters, hydrogen atoms in idealized positions with a 1.2-fold isotropic U-value of the equivalent U value of the corresponding C-atom. $R1$ = 0.0434, $wR2$ (all data) = 0.1041, GooF(F^2) = 1.084, $w^{-1} = \sigma^2(F_o^2) + (0.0607P)^2$, where $P = [(\max F_o^2, 0) + 2F_c^2)]/3$, maximum/minimum residual electron densities 0.789 and −0.312 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CSD 380154. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int code +(1223)336033; e-mail: teched@chemcrys.cam.ac.uk).

(20) The Gaussian 94, Revision D.1, was used. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian, Inc.*, Pittsburgh, PA, 1995.

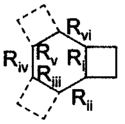
(21) (a) Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102. (b) See reference in footnote 10.

Table 2. Geometrical Parameters of Benzotricyclobutadiene at Different Theoretical Levels



	HF/ 3-21G	HF/ 6-31G*	B3-LYP/ 6-31G*	HF/ 6-311G**	MP2/ 6-31G*
R_1	1.5234	1.4999	1.5128	1.5002	1.5085
R_2	1.3093	1.3173	1.3379	1.3161	1.3439
R_3	1.5033	1.4837	1.4738	1.4837	1.4700
R_4	1.3478	1.3447	1.3750	1.3449	1.3812

Table 3. The Six-Membered Ring Bond Lengths in the Free Ligand (3 and 5, B3-LYP/6-31G*) and in the Iron Complexes (4 and 7, X-ray Determination)



parameter	**3**	**4**	ΔR_n	**5**	**7**	ΔR_n
R_i	1.4247	1.439(4)	+0.014	1.5128	1.480(5)	−0.033
R_{ii}	1.3614	1.427(5)	+0.066	1.3379	1.449(6)	+0.111
R_{iii}	1.4368	1.356(5)	−0.081	1.5128	1.456(6)	−0.057
R_{iv}	1.3785	1.442(5)	+0.064	1.3379	1.429(6)	+0.091
R_v	1.4368	1.356(5)	−0.081	1.5128	1.469(6)	−0.044
R_{vi}	1.3614	1.416(5)	+0.055	1.3379	1.451(6)	+0.113

et al. for other tris-annulated benzene systems.[21] The results for **5** (Table 2) show similar features.[22] Thus, for the geometrical discussions we will refer to the DFT-optimized geometries as the geometries of the free ligands.[23]

(iii) The Geometrical Effect of Complexing Fe(CO)$_3$ to Benzocyclobutadiene. Generally, substitution effects are additive in chemistry. Viewing tricarbonyliron as a benzocyclobutadiene substituent we ask what should be the bond lengths of the six-membered ring in **7** if the geometrical effects of complexing Fe(CO)$_3$ are additive? The free ligand **3** is localized in the Mills−Nixon manner, whereas in its Fe(CO)$_3$ complex (**4**) it is localized in the other direction. Since **5** is much more localized than **3**, but **7** has three Fe(CO)$_3$ moieties, it may be assumed that these effects cancel out. However, a closer look reveals that this argument does not hold. Thus, the sum of the bond lengths of the six-membered ring in **3** is 8.400 Å (theoretical), whereas in **4** it is 8.437 Å (experimental). The corresponding sums for **5** and **7** are 8.552 and 8.734 Å, respectively. Thus, whereas the six-membered ring bonds lengthen only a little (0.037 Å) when going from **3** to **4**, the respective bonds in **7** vs **5** lengthen quite considerably (0.182 Å), more than 1.5 times that is required from complete additivity.[24] The nonadditivity becomes even more pronounced when individual bonds are examined. The geometrical differences between **3**, **4**, **5**, and **7** are given in Table 3. Two features are obvious; the first is that the four-membered ring equalizes its bond lengths upon complexation to the iron. Thus, whereas in the free ligand **3** R_1, R_5, and R_6 are considerably different (1.425, 1.525, and 1.352 Å, respectively, Table 1), they are much more similar in the complex (1.439, 1.456, and 1.470 Å, respectively). The second feature is that the alternation in the six-membered ring is reversed. R_{iii}, the longest bond in the free ligand, is the shortest in the complex.

Table 4. Optimized Geometries and Energies Benzotricyclobutadiene (B3-LYP/6-31G*) in Planar D_3h Geometry and in Bent (according to X-ray structure) Geometry

	planar	nonplanar
R_1	1.5128	1.5159
R_2	1.3379	1.3442
R_3	1.4738	1.4755
R_4	1.3750	1.3739
total energy[a]	−460.6304038	−460.6060943
relative energy[b]	0.0	15.25

[a] Hartrees. [b] kcal mol^{-1}.

For complete additivity, the "corrections" for complexing tricarbonyliron fragment to **3** are given in Table 3 (ΔR_n) and when applied to **5** should have given the geometry of **7**. The fused bond should be corrected by $\Delta R_i + \Delta R_{iii} + \Delta R_v$ and for the other bond the correction should be $\Delta R_{ii} + \Delta R_{iv} + \Delta R_{vi}$. These calculated numbers are −0.147 and +0.184 Å, respectively, whereas the respective experimental numbers (i.e., the change between the average respective bond lengths in **7** relative to **5**, ΔR_n Table 3) are −0.045 and +0.105 Å. Therefore, the 164% additivity found for the sum of the bond lengths[24] results from unequal contribution in the change of specific bonds (57% of the bonds that lengthen, 30% for the bonds that shorten). We therefore conclude that there is no additivity in the comparison **3** vs **4** and **5** vs **7**.

To examine the effect of the nonplanarity of the ligand in **7**, we have fixed the angles between the six- and the four-membered rings in **5** to the values found in **7** and reoptimized all the other parameters within B3-LYP/6-31G* theoretical framework. The effect of the deplanarization of the geometry was found to be rather small (Table 4). Further investigation of the nonplanarity effect was carried out by calculating bent **3** with bending angles taken from the structure of **7** (i.e., 12.8, 19.2, and 20.2 degrees) and reoptimizing all the other parameters. The results are given in Table 5. The energy associated with the bending is minimal; thus, the energy cost of the highest bending (20.2°) is only 5.6 kcal mol^{-1}. Interestingly, the energy of bending is also not additive. Adding the contribution of each of the "bent **3**" is summed to 12.9 kcal mol^{-1} whereas bending of the rings in **5** in the same respective angles costs 15.3 kcal mol^{-1}, i.e., 119% additivity.[25] We thus conclude that generally, the effect of complexing Fe(CO)$_3$ to a benzocyclobutadiene is not additive, and the deplanarization of **7** is not accounted for this nonadditivity. There must therefore be an electronic effect (or effects) that is basically different between the complexes **4** and **7**.

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(22) The geometry of **5** in D_3h symmetry is a real minimum on the potential surface. This was verified by frequency calculations and by starting the optimization in C_1 symmetry.

(23) Frank, Baldrige, and Siegel (ref 21) have shown that experimental geometries of tris-annulated benzene systems are well reproduced within a similar theoretical level. Here it is shown that qualitative considerations also agree that the geometris of **3** and **5** are best described within B3-LYP/6-31G* level of theory. Thus, when comparing geometrical parameters it is quite safe to use data that was obtained within this level of theory.

(24) For complete additivity, the bond lengthening between **5** and **7** should be 3 × 0.037 = 0.111 Å. Therefore, 164% additivity is found.

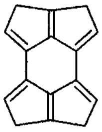
(25) Substitution effects are partially additive in organic chemistry. For example, $CH_3CH_2^+$ and $(CH_3)_3C^+$ are more stable than CH_3^+ by 36 and 72 kcal mol^{-1}, respectively. Thus, the additivity of the methyl stabilization effect is 66.7%. The fact that the "additivity" here is more than 100% suggests some synergistic effect rather than simple additivity.

Table 5. Optimized Geometries and Energies of Benzocyclobutadiene at Different Bending Angles. Θ = Angle between the Six- and Four-Membered Rings

	planar	Θ = 12.8	Θ = 19.2	Θ = 20.2
R_1	1.4247	1.4239	1.4233	1.4232
R_2	1.3614	1.3642	1.3675	1.3682
R_3	1.4368	1.4343	1.4313	1.4307
R_4	1.3785	1.3802	1.3820	1.3823
R_5	1.5245	1.5266	1.5289	1.5293
R_6	1.3518	1.3509	1.3499	1.3498
total energy[a]	−308.3603335	−308.3567286	−308.352316	−308.3514757
relative energy[b]	0	2.26	5.03	5.56

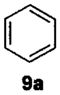
[a] Hartrees. [b] kcal mol^{-1}.

(iv) The Electronic Effect of Complexing $Fe(CO)_3$ to Benzocyclobutadiene. Examining the geometry of the tris(cyclobutadieno)benzene moiety in **7** reveals that the bonds are much longer than expected from an aromatic system. Using Pauling bond order formula,[26] we find that the average bond order for the free ligands (i.e., **3** and **5**) is 1.58. This does not change much in the mono-iron complex (in **4** the average bond order is 1.55), but it changes considerably in **7**, where the average bond order is 1.31.[27] This indicates that the central six-membered ring in **7** cannot be regarded as a benzene (or cyclohexatriene) but rather as consisting of bonds with a high character of single bonds. The ^{13}C chemical shift of the six-membered ring carbon atoms in **7a** (59.4 ppm) support this conclusion; it is 37 ppm upfield from the respective carbon resonance in **4**,[28] and ca. 60 ppm upfield from usual aromatic carbon chemical shift. Furthermore, the bond lengths in the six-membered ring of **7** reminds much more those of **8**[29] (where the bond lengths in the six-membered ring range between 1.44 and 1.452 Å), rather than a structure of an aromatic molecule.



8

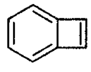
To shed some more light on the electronic structure of the systems, we have carried out NRT[30] analyses of **3** and **5** at optimized geometries and at geometries of the ligand in **5** and **7**, respectively.[31] This gave a quantitative resonance picture of the systems under study. For comparison we calculated benzene (the parent aromatic systems) using the same theoretical procedure. The two dominant structures are **9a** and **9b**, each contributes 43.1%. All the other 126 resonance structures contribute a total of 13.7%, each less or equal to 0.9%.



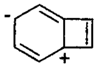
9a

9b

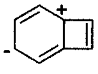
For **3**, the dominant resonance form is **10a**, which contributes 56.2% of the structure. There are eight more structures, (**10b**−**e**), all charged, each contributing between 4 and 10%. All the other 62 resonance structures (including **10f**) contribute less than 1% each. Thus, the notion obtained from the geometry of **3**, i.e., that it is a bond-fixed system (in the Mills−Nixon manner) to a large degree is obtained also by quantitative resonance structures analysis. The benzocyclobutadiene ligand in **4** shows, however, a much more aromatic character, as reflected also by the NMR spectra of the complex.[15] The two dominant resonance structures are **10a** and **10f**,



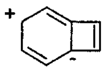
10a



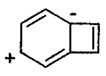
10bi



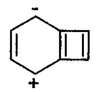
10bii



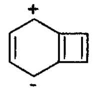
10ci



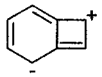
10cii



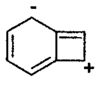
10di



10dii

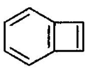


10ei

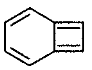


10eii

which contribute 41.5 and 31.8% (compared to 43.1% in benzene, see above) to the total structure, respectively (i.e., total of more than 73% of the structure). The structures **10b**−**e** contribute a total of 13.3%, all ranging between 1.4 and 3.1%. Among these, there is no definite preference to structures that have the double bonds in the 1−2 (the fused bond), 3−4, and 5−6 positions. However, the structure of the ligand (in the complex) implies that the resonance structures of the type **10f** should be preferred. Therefore, we conclude that the geometrical changes between **3** and the ligand in **4** are only partially reflected in the relative contributions of the resonance structures of the ligand. The complexation of the iron fragment to the four-membered ring probably stabilizes resonance structures such as **10f** and even **10g** (which contributes less than 0.1% in the optimized geometry as well as in the geometry of the ligand) that



10f



10g

are resonance structures of cyclobutadiene and therefore are high in energy in the noncomplexed fragments (thus

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[26] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1961; pp 239−240. For benzene (HF/6-31G* geometry) the bond order is 1.59.

[27] Average R_1 and R_2 (see Table 2 for definitions) bond orders: **3**: 1.42, 1.75. **5**: 1.09, 2.06. **4**: 1.66, 1.43. **7**: 1.23, 1.38.

[28] Shepherd, M. K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 961.

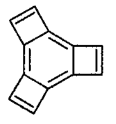
[29] Kono, Y.; Miyamoto, H.; Aso, Y.; Otsubo, T.; Ogura, F.; Tanaka, T.; Sawada, M. *Angew. Chem.* **1989**, *101*, 1254. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1222.

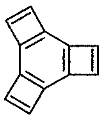
[30] NRT abbreviates Natural Resonance Theory. NBO 4.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1996.

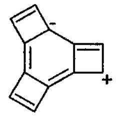
[31] Within HF/6-31G* level of theory.

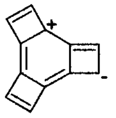
not contributing much to the molecular structure) but are stabilized due to the complexation to the Fe(CO)$_3$.[9]

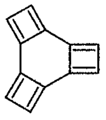
The same phenomena, and even more pronounced, are observed in the study of **5** and the free ligand of **7**.[32] Thus, for **5** the dominant resonance structure is **11a**, which makes 43.4% of the structure. This percentage is very similar to the respective structure in benzene (i.e., **9a** or **9b**), but the other respective structure (**11b**) contributes less than 0.1%. As suggested by the geometry, this molecule should be regarded as a cyclohexatriene fused to three cyclobutene rings. There are six structures of the type **11c**, and six of the type **11d**, contributing each 3.4 and 1.9%, respectively. Therefore, 74.2% of the structure of **5** is described by these 13 structures, none containing a double bond in the fused bonds. Clearly, this system is nonaromatic. However, when the free ligand is analyzed (in its geometry as a ligand), **11a** is only 29.5% of the structure. The twelve structures **11c** and **11d** make 51.7% of the total structure. In contrast to the case of benzocyclobutadiene, where changing the geometry of the molecule to the geometry of the ligand in **4** causes more delocalization, in the tricyclobutadienic system the change to the geometry of the ligand decreases the double bond character of the exocyclic bonds *without enhancing the double bond character of the endocyclic bonds*. This is coherent with the picture obtained from bond order analysis (see above). The structures of the cyclobutadiene moieties in **7** (i.e., **11b** and **11e**) contribute less than 0.1%, although evidently they are important to describe the structure of the complex. The effect of binding the Fe(CO)$_3$ fragments (as was observed in **3** and **4**, but enhanced) is to stabilize **11b** and **11e** that therefore contribute relatively more to the structure of **7**. The nonadditivity discussed before regarding the geometry of the systems manifests itself also in the resonance picture.


11a


11b


11c


11d

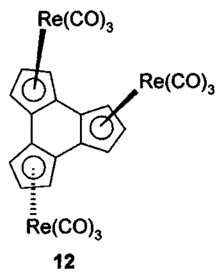

11e

(v) Energetic Considerations. To the best of our knowledge, bond dissociation energies for Fe–cyclobutadiene derivatives are unknown. The closest relevant measure is the energy of the bond between Fe(CO)$_3$ and 1,3-butadiene, which is 48.5 kcal mol^{-1}.[33] This should at least compensate for the energy cost of deforming the ligand from its optimized geometry to its geometry in the complex. Indeed, this energy difference for **5** is 105.5 kcal mol^{-1} (HF/6-31G*), which is 41.7 kcal mol^{-1} less than the minimum requirement (i.e., three times Fe–butadiene bond energy). However, deforming **3** to its geometry in the complex requires 128.0 kcal mol^{-1} (HF/6-31G*), much more than is given by the (CO)$_3$Fe–1,3-butadiene bond energy. Thus, there is additional stabilization in this complex. This probably comes from the resonance energy associated with cyclobutadiene–Fe(CO)$_3$ complex, estimated (theoretically) to be ca. 13–50 kcal mol^{-1}.[9] Clearly, even the highest estimate is not enough to compensate for the deformation of the ligand. Therefore, it is concluded that the stabilization of **4** by resonance is at least 79.5 kcal mol^{-1}, i.e., more than associated with the respective stability of benzene (ca. 60 kcal mol^{-1}), probably because in **4** the binding of the (CO)$_3$Fe allows also aromatization of the benzene moiety. These results also imply that the Fe–cyclobutadiene bond in **7** is stronger than that in **4**, and consequently, the use of the complex as a deliverer of cyclobutadiene[34] will be much less effective in **7** than in **4**. This point is currently under investigation.

The deformation of **3** to its geometry in **4** is much more endothermic than the respective deformation in **5**. An explanation can be obtained from the resonance picture outlined above. The deformation in **5** lowers the contribution of the resonance form **11a** without mixing new forms such as **11b** and **11e**. In **3**, the deformation to the geometry of the ligand in **4** involves a considerable mixing of **10e**. Thus, the structure contains mainly the two structures **10a** and **10e** that include the structure of singlet cyclobutadiene–an unstable moiety.

(vi) Mills–Nixon Effect. As shown above, the tris(cyclobutadieno)benzene ligand in **7** cannot be regarded as aromatic (or cyclohexatrienic), and the bond connecting the four-membered rings are best regarded as single bonds. Thus, the effect of localization by strain, if found, is expected to be small.

A comparison of **7** to an analogous systems, having rings larger than cyclobutene annulated to the six-membered ring, should give an indication whether strain plays a role in determining the geometry of **7**. One such structure was found, that of *trans*-[Re(CO)$_3$]$_3$(trindenyl) (**12**).[35] The electronic similarity between **7** and **12**, the similar arrangements of the metal fragments (i.e., trans), the similar deviations of the annulated rings from coplanarity with the planar six-membered ring, and the similarity of the bond lengths in the six-membered rings in the two complexes suggest that these two systems are comparable. In **12**, a small "anti-Mills–Nixon" effect is found, with average endo- and exocyclic bond lengths of



12

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[32] For easier analysis that could be compared to these of the other systems under study, average bond lengths for the endo- and exocyclic bonds (to the four-membered rings) were taken in a planar geometry (D_3h symmetry). A similar calculation of the ligand in its exact geometry as taken from the X-ray structure shows similar results; **11a** contributes a similar amount, and the sum of the twelve structures **11b** and **11c** (each contributing a slightly different amount) is similar to that of the system calculated in D_3h symmetry.

[33] Connor, J. A. *Topics Curr. Chem.* **1975**, *71*, 71–110.

[34] Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.

[35] Lynch, T. J.; Helvenston, M. C.; Rheingold, A. L.; Staley, D. L. *Organometallics* **1989**, *8*, 1959.

1.440 and 1.451 Å, respectively.[36] Another relevant comparison is to the triphenylene system, where the central six-membered ring is substituted by three benzene moieties. Both X-ray[37] and electron diffraction[38] studies agree that the bonds in the central ring are relatively long and that the system shows a small anti-Mills−Nixon effect (0.032 and 0.058 Å, respectively). Thus, it is concluded that the effect of strain of the four-membered ring in **7** manifests itself by fixing the bonds in a Mills−Nixon manner, relative to less strained systems.

(vii) Summary. The structure of **7** and the theoretical calculations presented above show that the molecule is best described as three tricarbonyliron−cyclobutadiene complexes connected by single $C_{sp^2}-C_{sp^2}$ bonds. All the evidence show that the six-membered ring cannot be treated as a substituted benzene or cyclohexatriene, but rather it is a spectator to three cyclobutadiene complexes. Structural comparison with **12** and triphenylene suggests that the four-membered ring localizes (albeit only to a small extend) the six-membered ring in a Mills−Nixon manner, as was predicted by theory.[10c] Clearly, aromaticity−antiaromaticity factors are not present in **7**, as the competition for the π electrons are between the benzene moiety and the cyclobutadiene−iron moieties, where the latter “win”, and the six-membered ring cannot be regarded as a substituted benzene. It seems that the structural features of **7** are governed mainly by the complexation to iron and by strain, where the delocalization of the 6π electrons in the six-membered ring plays a much less important role. Thus, if our results have implications regarding the origin of aromaticity, they support Shaik’s views.[3] Efforts are now being made to prepare other complexes of **5**, where the binding of the metal fragments will be η^2 to the external double bonds of the four-membered ring, leaving the three double bonds of the central six-membered ring uncomplexed.

Experimental Section

The Preparation of Tris(tricarbonylironcyclobutadieno)benzene (7). A slurry of hexabromotricyclobutabenzene (19 mg, 0.03 mmol) and diiron nonacarbonyl (200 mg, 0.55 mmol) in pentane (20 mL) was stirred at rt for 20 h. The slurry was filtered, and the filtrate was evaporated to dryness. The crude product was charged on a silica column, and the residue of the starting material was eluted with hexane. The product was obtained by elution with benzene. Recrystallization from hexane at −20 °C gave **7a** as red-orange prismatic crystals suitable for X-ray crystallography (3 mg, 5.3×10^{-3} mmol, 20% yield). Mp 147−148 °C. IR (KBr): 1975, 2040, 2062 (cm^{-1}) (C=O stretches). HRMS: *m/e*: Calcd 569.8060. Found: 569.8154. NMR (CDCl$_3$): ^{1}H 4.31 (s, 2H), 4.17 (s, 2H), 4.06 (s, 2H). ^{13}C 212.9, 61.9, 61.2, 59.4, 59.0.

Acknowledgment. We thank professor Sasson S. Shaik for helpful discussions and the Basic Research Fund administered by the Israeli Academy of Sciences and Humanities, The Fund for Promotion of Research at the Technion, Fonds der Chemischen Industrie, and Volkswagen Stiftung for financial support.

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[36] Although the σ values for **12** are rather large, it is clearly different from the structure of **7** in the discussed respect. To the best of our knowledge it is the only published structure of this type.

[37] Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16,* 503.

[38] Ferraris, G.; Jones, D. W.; Yerkess, J. *Z. Kristallog.* **1973**, *138,* 113.