

Evidence for metal induced bond localization in cyclobutabenzene: the crystal and molecular structures of η^6 -Cr(CO)₃ and η^4 -Fe(CO)₃ complexes of cyclobutabenzene

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Abstract

The crystal and molecular structure of the title compounds were determined at low temperatures. The accuracy of the structures allows for a discussion about the bond alternation in the six-membered ring. It was found that both complexes show bond localization, whereas the benzocyclobutene-Cr(CO)₃ shows localization in the Mills–Nixon effect manner, the benzocyclobutadiene-Fe(CO)₃ shows an anti-Mills–Nixon localization. © 1997 Elsevier Science S.A.

1. Introduction

The debate about the Mills–Nixon effect ranges over sixty years [1]. Although the basic concept of the original work was based on an equilibrium between two tautomeric structures, the term Mills–Nixon effect is used today to describe the effect of σ strain on the structure of the aromatic skeleton¹. In 1991 one of us published a theoretical investigation regarding the Mills–Nixon effect [3]. The conclusions and predictions of this study were the following: (a) Strain imposed on an aromatic ring causes bond localization. (b) There is a quantitative relationship [4] between the bond localization and the bond angle. (c) Systems that have rehybridizable carbon atoms at the strained positions will

form curved bonds, so that the effective bond angles (formed by the maximum electron densities paths) are larger than the angles formed by the respective linear C=C bonds. This is the reason why (for example) tricyclobutabenzene (1) shows only a small bond fixation, although the apparent bond angles are smaller than 94°. (d) For systems which should show some bond fixation, non-rehybridizable carbon atoms are necessary in the strained positions.

During the last two years some of these predictions were experimentally confirmed. Boese et al. measured the solid state structure and the X–X-electron deformation density of 1 [5], and showed that indeed the bonds are curved, and the effective bond angles correlate well to the difference between the long and short bonds in the six-membered-ring by our formula [4]. The second evidence was given by Bürgi et al. They have used the bridgehead carbon atoms of a bicyclic moiety as non-rehybridizable carbon atoms, and indeed the structure of 2 shows significant bond localization in the six-membered ring [6]. The measured ΔR is 0.089 Å, which correlates by our formula [4] to a bond angle of 103.3° ($\alpha \approx 16.7^\circ$). The measured bond angle is 103.3° [6], indicating a remarkable agreement between the theoretical model [3] and the experimental finding [6], and that the concept of

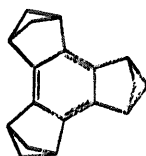
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¹ We fully agree with Professor Siegel (see Ref. [2]) that the term Mills–Nixon effect should be changed. However, as the term is still widely used in the literature to describe the effect of strain on localizing the bonds of an aromatic moiety we use it here to describe strain induced bond localization.

non-rehybridizable carbon atoms at the strained positions causing bond alternation really works.



1



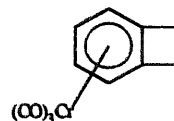
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In our theoretical work [3], we suggested that organometallic complexes of strained aromatic compounds should show bond alternation. Note, however, that the bond fixation is governed by the effective bond angles, and thus, any factor that influences the curvature of the bonds should influence the amount of bond fixation. Cremer and Kraka [7] had shown that the curvature of the bonds in three-membered rings is dependent by large on the electronegativity of the substituents (or heteroatoms), even to a degree of 'inverted banana bonds'. As some organometallic fragments are highly electronegative (especially $M(CO)_n$) [8], one may expect that the curvature of the bonds in the rings complexed to an $M(CO)_n$ fragment will not always be 'simple banana bonds' or non-curved bonds².

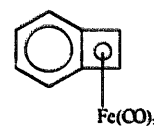
The organometallic fragment can be bound to the aromatic moiety, leaving the four-membered ring(s) out of the complexation sphere, or to a cyclobutadiene moiety (or moieties) fused to an aromatic ring, leaving the six-membered ring uncoordinated [10]. In both cases, no aromaticity–anti-aromaticity arguments can be involved [11] (as the π complexes are neither), and relevant carbon atoms are bound to a transition metal which makes them less rehybridizable than in the free ligand. Thus, if there is no dramatic difference in the electronic structure of the studied molecules, any bond localization (larger than expected by the normal substitution effect, and especially compared to the free lig-

ands) suggests that the strain affects the geometry of the aromatic moiety, i.e. the Mills–Nixon effect³.

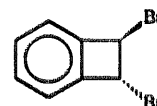
We report here the solid state structures of 3 and 4, both containing only one four-membered ring fused to a benzene moiety, but already showing evidence for the Mills–Nixon effect.



3



4



5

2. Results and discussion

The complexes were prepared according to literature procedures. In both cases we have used 1,2-dibromocyclobutabenzene (5) [12] as starting material. For the preparation of 3, 5 was reduced with $Bu_3SnCl/LiAlH_4$ [13] in 45% yield and then allowed to react with $(CO)_3Cr(CH_3CN)_3$ [14] to give 3 in 30% yield. For the preparation of 4, 5 was allowed to react with $Fe_2(CO)_9$ [15] to give 4 in 75% yield. 3 was crystallized from pentane (4°C), but since 4 is a liquid at RT, the crystallization was performed by means of a miniature zone refinement procedure in the capillary with an IR laser as the heating source, generally known as the in situ IR-laser crystallization technique [16]. Details of the low-temperature structure determination are given in

² Shaik et al. [9] have shown that the geometrical properties of isoelectronic species depend by large on their electron affinities and ionization potentials – properties that are related to electronegativity. Thus, it is documented that structural properties depend on the way that the systems attract electrons – not only for strained systems.

³ The Mills–Nixon effect is used here in the broader sense, i.e. as strain affecting bond localization. Thus, fixation of the bonds either in the Mills–Nixon manner or in the opposite direction (anti-Mills–Nixon effect) are effects of strain, and thus treated here as the Mills–Nixon effect.

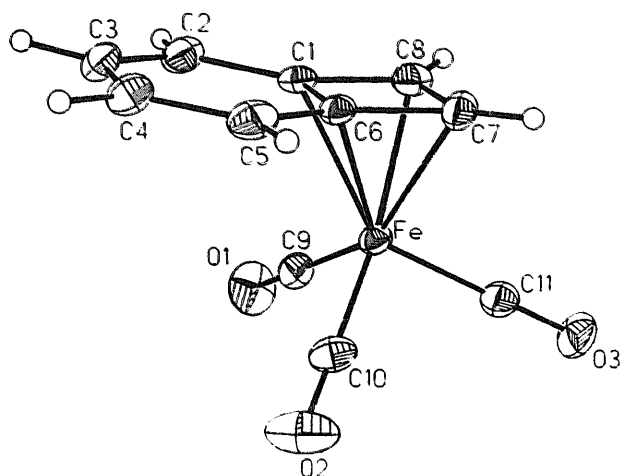


Fig. 1. Ellipsoid (50%) presentation of **4**.

Ref. [17] and Fig. 1 shows an ellipsoid presentation of the molecule.

The structure of tricarbonylchromium–benzocyclobutene had been reported before [18], but the errors in the geometrical parameters do not allow for a discussion about possible bond alternation. Other structures of $\text{Cr}(\text{CO})_3$ complexes of cyclobutabenzene have been determined [19], but as they are substituted, the geometrical parameters relevant to the discussion here are perturbed. The structure of **4** is undetermined as yet⁴. There are some relevant publications regarding benzocyclobutadienes and their complexes with tricarbonyliron [21–23], but these systems are heavily substituted and therefore their structural parameters may be affected (at least partly) due to steric congestion. Thus, in order to discuss the metal effect on bond localization in cyclobutabenzene, it was necessary to redetermine the structure of **3** at low temperatures and to determine the structure of the parent tricarbonyliron–benzocyclobutene.

Table 1 shows the bond lengths in the six-membered ring in $\text{Cr}(\text{CO})_3(\text{benzene})$ [24], cyclobutabenzene [25], **3** and **4**. The $(\text{CO})_3\text{Cr}(\text{benzene})$ shows distinct bond localization. The chromium, adopting a pseudo-octahedral coordination sphere is bound to the benzene ligand through three (coordinated) double bonds (those anti to the carbonyls) leaving three uncoordinated bonds. The bond lengths of those coordinated to the metal are 1.401–1.402 Å, i.e. almost the same as the free benzene bond lengths (1.400 Å), whereas the other three bonds are 1.419–1.420 Å. Thus, if the $(\text{CO})_3\text{Cr}$ –benzene complex is considered as the reference system for the effect of Cr on localizing the aromatic moiety bonds, we find

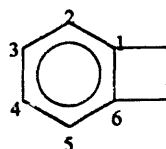
that a bond alternation of 0.018 Å is induced by the metal, and the main effect is lengthening the uncoordinated bonds. This effect is similar in other metal–arene complexes. For example, the six-membered ring in $(\text{CO})_3\text{Mo}$ –benzene shows average bond lengths of 1.400(3) and 1.424(3) Å for the coordinated and uncoordinated bonds, respectively [26]. In the $(\text{CO})_3\text{Mo}$ complex of trimethylsilylbenzene the average bond lengths are 1.391(7) and 1.429(9) Å for the coordinated and uncoordinated bonds, respectively [27]. A methyl (instead of trimethylsilyl) substitution somewhat shortens all the bonds, and $(\text{CO})_3\text{Mo}$ –methylbenzene shows average bond lengths of 1.382(9) and 1.409(6) Å for the coordinated and uncoordinated bonds, respectively [28]. In sterically congested systems, the behavior is somewhat different, as the complexation allows the system to reduce strain. Thus, hexaethylbenzene, shows bond lengths of 1.402(1) Å [29]. Average bond lengths of 1.425(4) and 1.417(4) Å for the $(\text{CO})_3\text{Cr}$ complex and 1.427(4) and 1.423(4) Å for the $(\text{CO})_3\text{Mo}$ complex for the coordinated and non-coordinated bond were observed. Here the coordinated bonds are shorter than the non-coordinated bonds, and the fact that the lengthening is more pronounced in the Mo complex (where the metal is more distant than in the respective Cr complex and more loosely bound) indicates a tendency to relieve steric strain. Other η^6 complexes of sterically congested arenes show a similar behavior [30].

The structure of **3** resembles a case that is between the ‘normal’ and sterically congested systems. A small but less significant⁵ bond localization in the six-membered ring is observed. The average coordinated bond length is 1.398(8) Å – very similar to the one of the benzene– $\text{Cr}(\text{CO})_3$ complex, and so are the uncoordinated bonds – 1.413(6) Å. However, compared to the free ligand, both types of bonds lengthen – similar to the complexes of sterically congested systems; the coordinated bonds by 0.012 Å, and the uncoordinated by 0.019 Å. This is because the binding of the metal to the six-membered ring (in particular to C(1) and C(6)) reduces the ability of these carbon atoms to efficiently rehybridize to form curved bonds. As a result, the average bond length difference in the complex is 0.015(6) Å. Thus, although the apparent bond localization in **3** is small, the comparison to the free ligand (in relation to benzene and its $(\text{CO})_3\text{Cr}$ complex) reveals a Mills–Nixon effect.

⁴ The structure of single substituted $(\text{CO})_3\text{Fe}(\text{cyclobutabenzene})$ was reported, but the uncertainty of the geometrical parameters is too large to allow for a discussion about bond alternation. See Ref. [20].

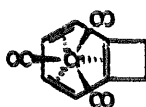
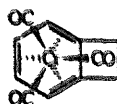
⁵ ‘Significant’ is used here in a simplified statistical sense, namely, $R(x)$ is significantly different from $R(y)$ if 3σ (the larger of the two) are added to the small R and it is still shorter than the long R . If the 2σ criterion is met only, data are generally accepted as different on a minor significance level and below 2σ no significance is assumed. The standard deviations of the mean values were calculated according to the statistical error propagation.

Table 1
Bond lengths of the six-membered ring in $(\text{CO})_3\text{Cr}(\text{benzene})$, cyclobutabenzene, **3** and **4**



	Benzenechromium–tricarbonyl	Cyclobutabenzene	3	4
C(1)C(2)	1.420(2)	1.381(2)	1.396(5)	1.416(5)
C(2)C(3)	1.401(1)	1.396(2)	1.426(6)	1.356(5)
C(3)C(4)	1.419(1)	1.397(2)	1.415(6)	1.442(5)
C(4)C(5)	1.402(2)	1.397(2)	1.404(6)	1.356(5)
C(5)C(6)	1.419(1)	1.381(2)	1.384(4)	1.427(5)
C(1)C(6)	1.401(1)	1.390(2)	1.408(4)	1.439(4)

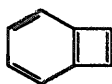
The conformation of the CO ligands relative to the cyclobutabenzene is also an indication for bond localization in the latter. Thus, the chromium adopts a pseudo-octahedral coordination sphere, which suggests that it is bound through the π bonds *anti* to the carbonyls. Indeed, $(\text{CO})_3\text{Cr}$ complexes of systems that are bond localized as free ligands (e.g., biphenylene [31], angular [3]phenylene [32], and star-phenylene [33], where a substantial rotational barrier around the Cr-arene axis was measured) show this *endo* bonding even when steric considerations would suggest that the *exo* rotamer is more stable. In cyclobutabenzene complexes of $\text{Cr}(\text{CO})_3$, the two rotamers are found in different systems [18,19], i.e. structures of the type **3a** and **3b**. We find only the rotamer **3b**. This implies that the bonds C(1)–C(2), C(3)–C(4) and C(5)–C(6), those which should be shorter according to the Mills–Nixon predictions, have a more pronounced double bond character than the other three bonds. These results are in full agreement with ^{13}C J coupling experiments on a substituted $(\text{CO})_3\text{Cr}$ -cyclobutabenzene system [34]. The binding of the Cr to the three bonds mentioned above allows to consider the metal binding to the six-membered ring which is not also η^2 to the four-membered ring [10].

**3a****3b**

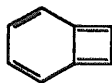
In **4**, the bond fixation is even more pronounced, however, reversed compared to **3**. Thus, clearly the C(2)C(3) and C(4)C(5) bonds are the shortest in the six-membered ring. The four-membered ring is a cyclobutadiene complex (bond lengths 1.439–1.470 Å, the shortest is the common bond of the four- and six-membered rings). Thus, the predominant resonance structures of the ligand in **4** are **6a** and **6b**, whereas in the free ligand the predominant resonance structure is **6c**⁶. The average bond length of C(1)C(2), C(3)C(4) and C(5)C(6) in **4** is 1.428(7) Å, whereas the average bond length of the other three bonds is 0.044 Å shorter, although it includes the longest C(1)C(6) bond. Even more striking is the difference between the six-membered ring bonds in cyclobutabenzene and **4**; whereas the C(1)C(2), C(3)C(4) and C(5)C(6) bond lengthen by an average of 0.039 Å, the other three bonds shorten by an average of 0.010 Å. Clearly, all the evidence suggest an ‘anti-Mills–Nixon’ effect. To verify that this effect is not only because of η^2 binding of the metal to the six-membered ring [10], the geometry of **4** has been compared to some η^2 -benzene complexes. In all cases that we have found (mono- η^2 complexes [35,36], bis-1,3- η^2 complexes [37], and tris- η^2 complexes [35,38]) the localization of the six-membered ring is in the same direction as was found for **4** (i.e., the non-coordinated bonds are shorter than the coordinated ones) but with a completely different magnitude. This is best illustrated by comparing the geometry of **4** to the η^2 -benzene complex with a Ru_6 cluster [35]; the bond length of the coordinated bond (the parallel to C(1)–C(6)) is 1.37 Å, i.e. shorter by 0.07 Å than the respective bond in **4**. All the other bonds are 0.02–0.07 (average 0.05) Å longer

⁶ (a) Based on ab initio theoretical calculations. (b) The structure of heavily substituted benzocyclobutadiene and its $\text{Fe}(\text{CO})_3$ complex was determined. See Refs. [21–23].

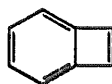
than in **4**. Thus, clearly the localization effect found in the six-membered ring of **4** cannot be attributed only to the η^2 bonding of the metal, and the four-membered ring has a considerable effect in the resulting geometry.



6a



6b



6c

The NMR chemical shifts of **4** suggest that (at least to a large part) the six-membered ring is still aromatic. Thus, the ^{13}C chemical shifts of the four carbon atoms not fused to the four-membered ring (i.e. C(2)–C(4)) are 124.2 and 127.4 ppm, and the ^1H chemical shifts of the respective protons are 7.05 and 6.88 ppm. We are currently investigating the reasons for this bond localization, and preparing similar complexes of tricyclobutabenzene in order to investigate the phenomena in extended systems, where the metal complexation effect should be more pronounced.

Acknowledgements

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