J|A|C|S
ARTICLES
Published on Web 09/13/2002

Effective Aromaticity of Tricarbonylchromiumbenzene, about 25% Enhanced over that of Benzene: Structural Evidence from a Complexed Benzannulene

Reginald H. Mitchell,*,† Zinka Brkic, David J. Berg,* and Tosha M. Barclay‡

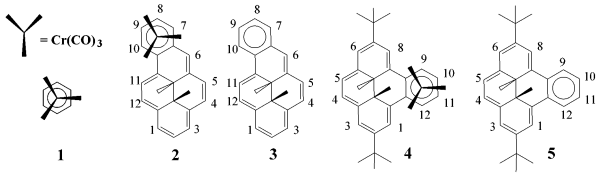
Contribution from the Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

Received May 17, 2002

Abstract: The tricarbonylchromium complex of 2,7-di-*tert*-butyl-*trans*-12c,12d-dimethylbenzo[*e*]dihydropyrene is prepared in 65% yield from the parent annulene. Analysis of the ^{1}H NMR spectrum leads to coupling constant data and Günther's "*Q*" value data which unequivocally indicate that the tricarbonylchromium-benzene moiety behaves like an aromatic system of greater bond fixing ability, aromaticity, than benzene itself; this analysis is supported by X-ray structural data and by the rotational position of the tricarbonyl podal. Analysis of chemical shift data indicates that the tricarbonylchromium benzene moiety has about 25% enhanced "aromaticity" over that of benzene.

Introduction

The recent issue of *Chemical Reviews*[1] devoted to "Aromaticity" indicates that this topic continues to fascinate a wide range of chemists. In 1990, we[2] first made the claim that tricarbonylchromium benzene, **1**, appeared to be more aromatic than benzene itself, because, in the fused complex **2**, the complexed ring had a larger bond fixing effect on the annulene ring than did the corresponding benzene ring in **3** and so reduced the ring current in the annulene ring to a greater extent. In 1996,



Simion and Sorensen[3] challenged this interpretation, on the basis of exaltation of diamagnetic susceptibility calculations and stated that **1** should be regarded as *anti*-aromatic. We disagreed and, in 1998, showed[4] that NMR data conclusively supported the idea that **1** and a variety of related organometallic complexed systems when fused to other aromatic systems behaved as aromatic rings themselves, which resisted bond fixation more strongly than did benzene and correspondingly caused more bond fixation in the adjacent fused ring than did benzene itself. In 2000, Schleyer with Simion and Sorensen[5] applied a refined NICS (Nucleus Independent Chemical Shift) method to **1** and, while not formally supporting our position, did finally state that "$Cr(CO)_3$ complexation does not reduce the aromaticity of benzene."

In this paper, by synthesis of the complexed annulene **4** and its comparison to **5**, we are now able to supply further more extensive NMR data and as well structural data to support our position.

Results

The reaction of benzannulene **5**[6] with tricarbonylchromium naphthalene[7] (**6**) in dry deoxygenated THF for 27 h at reflux gave a 65% yield of the complex **4** as dark reddish-purple crystals, mp 172−174 °C. These gave ^{13}C and ^{1}H NMR spectra consistent with the structure (see later text for details) and correct high-resolution mass spectral data for $C_{33}H_{34}CrO_3$ (found, 530.1911; calcd, 530.1913), as well as an X-ray structure (later text). Since accurate coupling constants were required, the proton and carbon spectra were acquired at 360 (90.6) MHz using considerably expanded data sets, such that the Hz/pt was reduced below 0.03 (^{1}H), and they were fully assigned by using 2D COSY, NOESY, and HMQCB (long and short-range couplings). Fortunately, from the pioneering work of McGlinchey[8] on the diamagnetic anisotropy of organometallic species, we previously[4] were able to assign the internal methyl protons of **2**. The methyl protons proximal to the $Cr(CO)_3$ group are deshielded relative to the distal ones. In the case of **2**, this effect is not very large, 0.11 ppm, but in the isomer of **2** in which the methyl

† Reginald Mitchell. Telephone: 250-721-7159. Fax: 250-721-7147. E-mail: regmitch@uvic.ca.
‡ Department of Chemistry, North Harris College, Houston, TX 77073.

(1) von Ragué Schleyer, P. (Guest Editor) *Chem Rev.* **2001**, *101*, 1115−1566.
(2) Mitchell, R. H.; Zhou, P.; Venugopalan, S.; Dingle, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 7812−7813.
(3) Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **1996**, *118*, 7345−7352.
(4) Mitchell, R. H.; Chen, Y.; Khalifa, N.; Zhou, P. *J. Am. Chem. Soc.* **1998**, *120*, 1785−1794.
(5) von Ragué Schleyer, P.; Kiran, B.; Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **2000**, *122*, 510−513.
(6) Mitchell, R. H.; Ward, T. R. *Tetrahedron* **2001**, *57*, 3689−3695.
(7) Desobry, V.; Kundig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288−1297.
(8) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104−109.

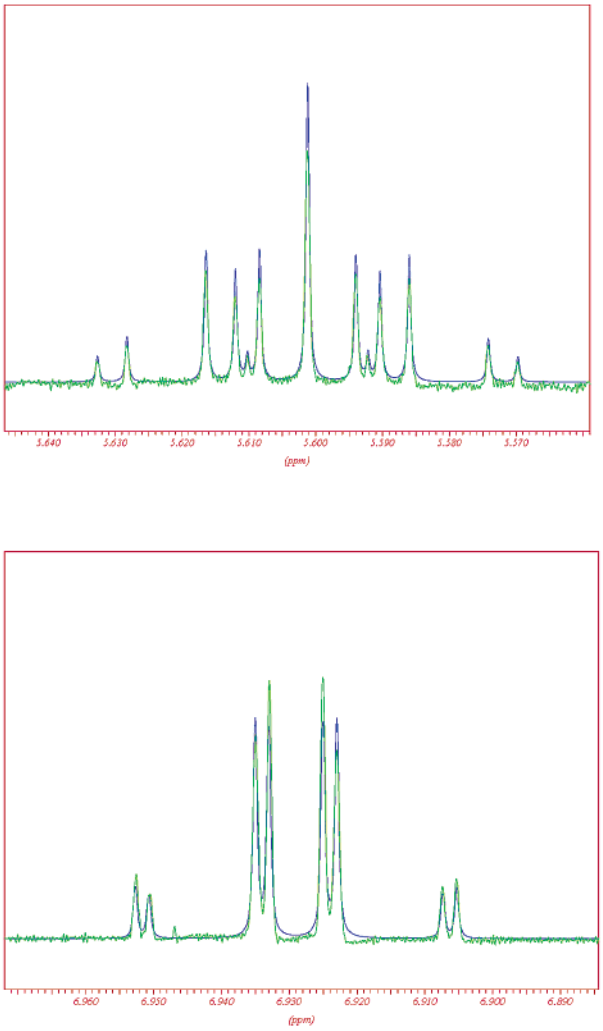


Figure 1. Experimental (green) and simulated (blue) ^{1}H NMR spectra for H-10,11 (top) and H-4,5 (bottom) of complex **4**.

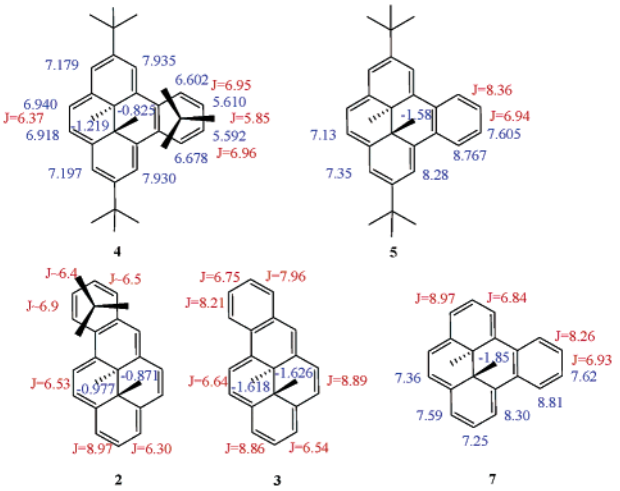


Figure 2. Proton chemical shifts (blue, ppm) and $^3J_{vic}$ coupling constants (red) for complex **4** and selected comparison molecules.

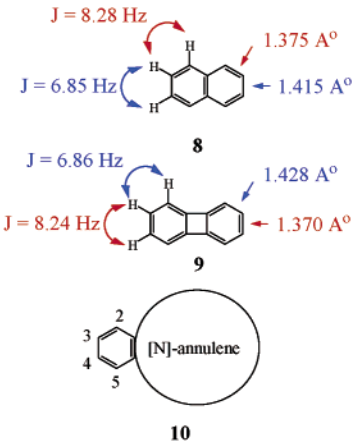


Figure 3. Coupling constants and bond length data for naphthalene[12] and biphenylene.[13]

groups are interchanged such that the proximal methyl is closer to the $Cr(CO)_3$, the effect is larger at 0.35 ppm. In **4**, the proximal methyl protons are even closer to the $Cr(CO)_3$, and the difference in chemical shift between the two methyl groups is 0.394 ppm. The proximal methyl protons are, thus, assigned to δ −0.825, and the distal methyl protons, to δ −1.219. From the ^{1}H−^{13}C HMQCB spectra, the bridge carbons attached to these methyl groups, and then similarly the 1,8 and the 3,6 protons, and, hence, the 9,12 and the 4,5 protons, and finally the 10,11 protons, and then each attached carbon could be assigned. In this way, it was possible to assign unambiguously all the important protons, such that the $^3J_{vic}$ couplings could be determined. In reality, this was easier said than done, since each of the 10 aromatic hydrogens is different and there are several small long range couplings. The least coupled protons were H-4,5 and H-10,11, and so, these were iterated first, with the other hydrogens added in, such that finally the whole 10 spin system was iterated and simulated. The expanded simulated and experimental spectra overlay each other extremely well, and examples are shown in Figure 1 for H-4,5,10,11; the remainder are available in the Supporting Information. Only H-1,8 remained slightly out, probably because of one or more small long-range coupling errors; however, by making changes to the important *ortho* ($^3J_{vic}$) coupling constants, we are satisfied that these have been determined with reasonable accuracy (±0.05 Hz). The results of our analysis are shown in full in the Experimental Section, but selected data are shown in Figure 2 together with that of **5**, **2**, **3**, and **7** for comparison.

The fusion of two aromatic rings along a common side causes bond fixation in both rings and leads to alternating bond lengths and coupling constants.[9−11] The alternating coupling constants can easily be seen for **3, 5**, and **7** in Figure 2 and, together with bond length data, are shown for naphthalene and biphenylene in Figure 3. Günther[9] has clearly established that when two ($4n + 2\pi$)-annulenes are fused as in naphthalene (**8**) or the benzannulenes **3, 5**, or **7**, then the C2−C3 bond of **10** is shorter and has a larger coupling constant than that of the C3−C4 bond. In a ($4n\pi$)-annulene such as biphenylene (**9**), which can be considered to be a fusion of an 8π to a 6π system, the reverse is true; the C3−C4 bond is shorter and has the larger coupling constant. Clearly, inspection of the data for **4** and **5** (Figure 2) indicates that both molecules fit into the ($4n + 2\pi$)-annulene group, the aromatic group, like benzobenzene (naphthalene, **8**), and suggests that both fused systems, the [14]annulene and

(9) Cremer, D.; Günther, H. *Liebigs Ann. Chem.* **1972**, *763*, 87−108.
(10) Günther, H.; Shyoukh, A.; Cremer, D.; Frisch, K. H. *Liebigs Ann. Chem.* **1978**, *78*, 150−164.
(11) Mitchell, R. H. *Chem Rev.* **2001**, *101*, 1301−1315.

the tricarbonylchromium-complexed benzene, of **4** are aromatic. Günther quantified this analysis by proposing that his "Q" value,[9] the ratio of bond orders $P_{2,3}/P_{3,4}$ in **10**, is > 1.14 when the [N]annulene is aromatic and < 1.03 when the annulene is antiaromatic. Since Günther found that SCF bond orders can be related to coupling constants by eq 1,

$$P_{n,m}\,(\mathrm{SCF}) = 0.104\,{}^{3}J_{n,m} - 0.120 \qquad (1)$$

an experimental comparison with calculated bond orders may be made.

For a benzo[14]annulene of the geometry of **5**, Günther calculates $Q = 1.143$; use of the experimental coupling constants for **5** and eq 1 yields an experimental value of $Q = 1.194$ for **5**.[14] When the data for the complexed annulene **4** are used, $Q = 1.170$.[14] Clearly both systems must be regarded as aromatic. This analysis can of course be reversed, since each π-system exerts an effect on the other. Inspection of the coupling constant pairs in the 14-membered rings of **3** (8.86/6.54 and 8.89/6.64 Hz) and of **7** (8.97/6.84 Hz) gives Q values > 1 in the same sense as for case of the benzene ring probes [note that the smaller coupling constants are for $J_{2,3}$ (see numbering scheme structures **1**−**5**), and $J_{11,12}$ (**3**), and $J_{1,2}$ (**7**)]. The pattern of bond orders is maintained for the complex **2**, namely the smaller coupling constants are still $J_{2,3}$ and $J_{11,12}$, and for complex **4**, where only one J_{vic} is observed in the 14-membered ring; the value found, 6.37 Hz, is consistent with the $J_{11,12}$ value of **2** (6.53 Hz). This bond order pattern clearly indicates that both fused rings are aromatic in the complexes **2** and **4** and is totally different to that observed when one ring is antiaromatic, as for biphenylene (**9**) in Figure 3.[9,10]

X-ray Data. In our previous studies,[4] we were only able to obtain an X-ray structure of **2** to support the structural skeleton but could not obtain crystals suitable for accurate bond length determinations.

We are now able to report a detailed structure for the complex **4** obtained at 218 K on a crystal 0.26 × 0.50 × 0.53 mm^3 using graphite monochromated Mo Kα radiation. Full details are given in the Supporting Information, but the final R indices [$I > 2\sigma(I)$] were $R_1 = 0.052$ and $wR_2 = 0.121$.

An ORTEP diagram of **4** is shown in Figure 4, with half the equivalent internal bridge methyl groups eliminated (the crystal structure solves with four-half occupied methyl positions), and the important periphery bond lengths are shown along with those of **5**[15] for comparison in Table 1.

Clearly, in agreement with the coupling constant data, the bonds alternate in the same way around the periphery of **4** as they do in **5**. If tricarbonylchromiumbenzene were antiaromatic, bonds C9−C10 and C4−C29 would be short and C10−C11 and C28−C29 would be long; that is, the opposite alternation pattern to that found would be observed, and thus, the inescapable conclusion to both the NMR and X-ray data is that the tricarbonylchromium benzene fragment is aromatic. In fact

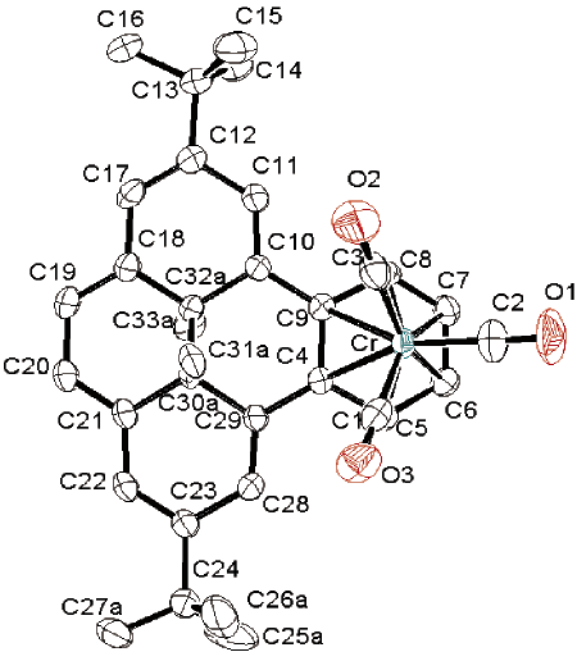


Figure 4. ORTEP diagram of complex **4** (50% thermal ellipsoids, H atoms omitted for clarity).

Table 1. Periphery Bond Lengths (Å) for **4** (218 K) and **5** (203 K)[15,a]

bond	4	5
C4−C5	1.441(5)	1.411(4)
C5−C6	1.388(5)	1.363(4)
C6−C7	1.410(5)	1.397(4)
C7−C8	1.396(5)	1.362(4)
C8−C9	1.438(4)	1.413(4)
C9−C10	1.472(4)	1.463(4)
C10−C11	1.352(5)	1.362(3)
C11−C12	1.454(5)	1.440(4)
C12−C17	1.360(5)	1.354(4)
C17−C18	1.431(5)	1.431(3)
C18−C19	1.356(5)	1.351(4)
C19−C20	1.426(5)	1.429(3)
C20−C21	1.362(5)	1.367(4)
C21−C22	1.414(5)	1.429(4)
C22−C23	1.360(5)	1.359(4)
C23−C28	1.453(5)	1.437(4)
C28−C29	1.344(5)	1.364(3)
C29−C4	1.470(4)	1.450(4)
C4−C9	1.438(5)	1.426(3)

[a] X-ray numbering.

since the average bond alternation (ΔΣ)[16] around the [14]-annulene ring of **4** (ΔΣ = 0.0905 Å) is greater than that around **5** (ΔΣ = 0.0804 Å), tricarbonylchromiumbenzene has an "effective aromaticity" greater than that of benzene itself, in agreement with our chemical shift results announced previously.[4,11] Interpretation of the bond alternation in the complexed ring of **4** is a little more difficult, since, even in tricarbonylchromiumbenzene (**1**) itself, the bonds are not equal. The bonds eclipsed by the carbonyl groups are about 0.02 Å longer than those not.[17] As well, in higher complexed arenes such as tricarbonylchromiumnaphthalene,[18] the Cr does not sit over the centroid of the benzene ring but slips toward the edge furthest

(12) (NMR) Reference 9. (X-ray) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1982**, *38*, 2218.
(13) (NMR) Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1982**, *239*, 345−351. (X-ray) Yokozeki, A.; Wilcox, C. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1974**, *96*, 1026−1031.
(14) This applies a 0.3-Hz correction to $J_{2,3}$ because of a "phenanthrene-like steric compression".[9,11] Without this correction, the value of Q is over estimated as 1.245 for **5** and 1.234 for **4**.
(15) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.*, in press.
(16) ΔΣ = (average long bond (Å)) − (average short bond (Å)). See Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907−2911.
(17) Rees, B.; Coppens, P. *Acta Crystallogr.*, Sect. B **1973**, *29*, 2515−2528.
(18) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* **1967**, *50*, 1052−1059.

from the ring fusion bond (that is, toward the C2−C3 bond in naphthalene).[19] However, in **4**, the slippage is toward the C7−C8 bond (Figure 4), which is away from the ring fusion bond and the proximal-methyl group: C4−Cr (2.284(3) Å) and C9−Cr (2.288(3) Å) are slightly longer than C5−Cr (2.192(4) Å) and C6−Cr (2.214(4) Å), which are slightly longer than C7−Cr (2.206(4) Å) and C8−Cr (2.204(4) Å), and presumably avoid steric interactions with methyl C31a. Indeed, a PCMODEL[20] molecular mechanics calculation actually simulates this slippage away from the fusion bond quite well, giving corresponding bond lengths to those above of 2.302/2.273, 2.205/2.182, and 2.200/2.229 Å respectively. In **4**, the eclipsed bonds are, thus, C9−C8, C7−C6, and C5−C4, which are already the longer bonds of the uncomplexed **5**, caused by fusion to the [14]-annulene, and thus, any additional lengthening because of the complexing might hide the reduction in alternation that would be expected if the complexed ring is harder to alternate than a benzene (that is, is more aromatic). However, as noted above, alternation in uncomplexed **5** ($\Delta\Sigma = 0.0905$) is still greater than that in complexed **4** ($\Delta\Sigma = 0.0804$), and this, thus, indicates that the [14]annulene must find it easier to localize benzene than complexed benzene!

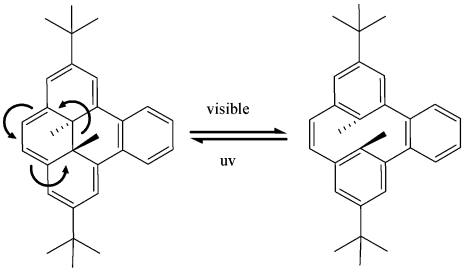
The rotational position of the tricarbonyl group may also be quite useful in suggesting the overall nature of the π-system. Atwood, Albright, and Rausch state[21] that in $4n\pi$ systems such as biphenylene, one carbonyl group eclipses the ring fusion bond, while, in $(4n + 2)\pi$ systems such as naphthalene, the ring fusion bond is not eclipsed. Indeed Siegel[22] finds supporting evidence for this in his star-phenylenes. Here, in **4,** clearly the ring fusion bond is not eclipsed, consistent with an aromatic-like system.

Aromaticity Index for Complex 4. We have extensively discussed the relative aromaticities of several organometallic moieties on the basis of chemical shift data for [*a*]-fused systems such as **2**.[4] In that paper, we found the relative bond fixing ability ("relative aromaticity") and the relative bond localizing energy of tricarbonylchromiumbenzene to be 1.27−1.28 times those of benzene itself. A referee suggested that we should give an aromaticity index value here also. However, in principle, this should be the same value as we observed before because the site of fusion of the tricarbonylchromium moiety on the dihydropyrene nucleus should not significantly affect the outcome (unless steric etc. effects come in to play). Moreover, the advantage of using the chemical shift data from the previous [*a*]-fused system **2** over the current [*e*]-fused system **4** to obtain this index is that the through space anisotropy effects of the tricarbonylchromium fragment in **2** are smaller ($\Delta\delta$(Me) = 0.106 ppm) than they are for the current **4** ($\Delta\delta$(Me) = 0.394 ppm). Nevertheless, if one inserts the δ(Me) values for **4** (−1.219 and −0.825) in eq 2, which is the best way to determine bond localization energies (BLE) in the [*e*]-fused annulenes,[6]

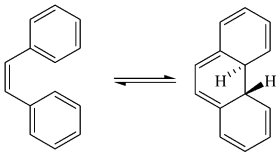
$$\mathrm{BLE} = 2.825 - [0.97 - \delta(\mathrm{Me})]^{0.643} \qquad (2)$$

then "relative aromaticity index" values of 1.37 and 1.17 are obtained, which average to 1.27, the same value obtained in the [*a*]-series. Anisotropy differences for H-4 (δ 6.918) and H-5 (δ 6.940) in **2** are less than those for the internal methyl protons, so if the average value for H-4,5 of 6.93 is used in eq 3, which converts H-4 chemical shifts into equivalent Me chemical shifts,[6] then a value of δ −1.073 for the Me protons of **2** is calculated (actual δ ($\mathrm{Me_{av}}$) = −1.022). Use of this calculated value in eq 2 then yields a value of 1.24 as the relative BLE for the tricarbonylchromiumbenzene fragment. Thus, on the basis of this work, the tricarbonylchromiumbenzene moiety has about 25% "more aromaticity" than benzene itself, or an aromaticity index of 1.24−1.27 relative to benzene = 1.00, in good agreement with our previous values.[4]

Photochromic Properties. All dimethyldihydropyrenes with an arene fused at the [*e*]-position that have been prepared so far are photochromic.[23] Irradiation of the dihydropyrene (DHP) form **5** with visible light rapidly opens the molecule to the cyclophanediene (CPD) form **11**. Irradiation of the colorless CPD form with ultraviolet light rapidly forms the colored DHP form. This is an example of the *cis*-stilbene (**12**) to dihydrophenanthrene (**13**) photoisomerization, studied by Muszkat and Fischer.[24]

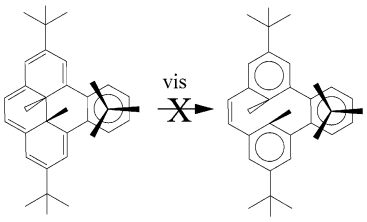


5 **11**



12 **13**

We wondered whether changing the aromaticity of the [*e*]-fused benzene ring by complexation would modify this photochromic behavior. Surprisingly, irradiation of a benzene-d_6 solution of complex **4** with visible light from a 500 W household tungsten lamp for 8 h, or when a 500 nm cutoff filter was used, did not yield any of the CPD form **14**. Under these



4 **14**

(19) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, 499−525.
(20) *PCMODEL*, version 7.00; Serena Software: Bloomington, IN 47402.
(21) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263−270.
(22) Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138−6142.
(23) Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, 2695−2703.
(24) Muszkat, K. A.; Gegiou, D.; Fischer, E. *Chem. Commun.* **1965**, 447−448. Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1967**, 662−678. Muszkat, K. A.; Eisenstein, M.; Fischer, E.; Wagner, A.; Ittah, Y.; Luttke, W. *J. Am. Chem. Soc.* **1997**, *119*, 9351−9360.

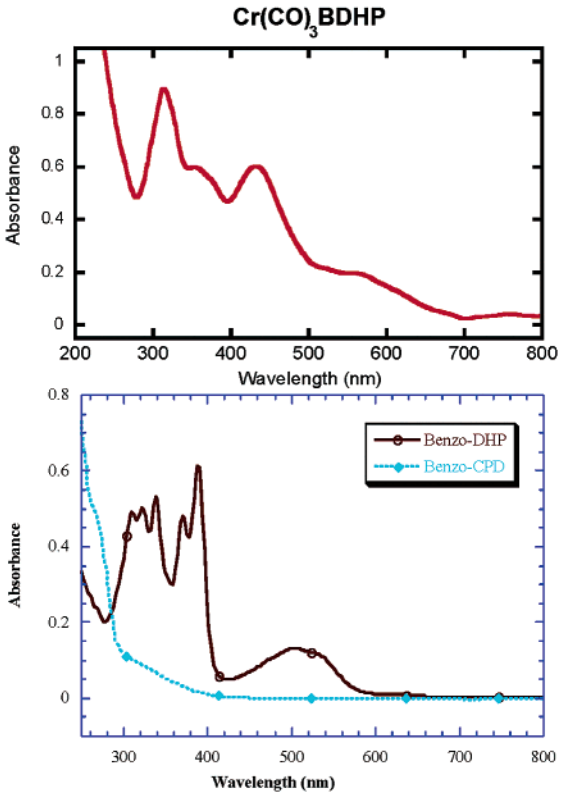


Figure 5. Upper: UV−vis spectra of Cr-complex **4**. Lower: UV−vis spectra of DHP **5** and CPD **11**.

conditions, the uncomplexed **5** was completely converted to **11** in just a few minutes. Very little decomposition of **4** occurred; the reaction appeared just not to go. There was no obvious reason to us for this failure. The difference in the heats of formation (ΔH_f) for **4**/**14** of 4.7 kcal/mol (the DHP form is more stable) is calculated to be smaller [25] than that for **5**/**11** (5.3 kcal/mol, DHP more stable) and in most of the cases studied,[23] isomerization is then faster, though even when this difference is much greater, isomerizations still proceed.[26] The absorption profile of complex **4,** shown in Figure 5, while different from that of uncomplexed **5**, shows absorption right out to 700 nm, and, thus, the complex should absorb the light. Cyclophane dienes have a tail absorption between 300 and 400 nm (see Figure 5), which does not normally interfere with the visible radiation isomerization. Tricarbonylchromiumbenzene[27] absorbs at 376 nm, so again it seems unlikely that **14** would immediately isomerize back to **4** with visible light irradiation. Whether this lack of isomerization has to do with the changed aromaticity of the complex or whether it has to do with the absorption profile or reaction intermediates will be perhaps better understood when we have more organometallic derivatives of **5** available. We will report in more detail on this in the future.

Conclusions

The increased bond alternation in the annulene ring of complex **4** relative to parent **5** as evidenced by bond length data, chemical shift, and coupling constant data, together with the coupling constant pattern (Günther's *Q* value) and rotational position of the tricarbonyl podal all show that tricarbonylchromiumbenzene is behaving as an aromatic system with greater bond localizing power, aromaticity, than benzene itself. Shift data suggest an "aromaticity index" of about 1.24−1.27 relative to benzene = 1.00. Whether theoreticians will agree that such complexes are aromatic remains to be seen, but given the mixed views on the meaning of the word "aromatic", we believe that if it measures up to the archetype, benzene itself, then it must be described as aromatic!

Table 2. Crystal Structure Data

formula	$CrO_3C_{33}H_{34}$
fw	530.60
crystal size, mm^3	0.26 × 0.50 × 0.53
crystal color	dark reddish-purple
crystal mount	on glass fiber with silicone glue
a, Å	19.369(9)
b, Å	16.082(7)
c, Å	17.955(8)
V, $Å^3$	5593(4)
cell detn, refls	370
d (calcd), g cm^{-3}	1.26
space group	*Pbcn*
Z	8
F000	2240
radiation	Mo Kα, graphite monochromated
λ, Å	0.710 73
temp, K	218
linear abs coeff, mm^{-1}	0.44
diffractometer	Smart 1000
scan technique	omega
2θ range, deg	4−50
h,k,l ranges	−23, 23; −19, 19; −21, 21
crystal decay, %	0.69
absorption correction	Sadabs
absorption range	0.81−1.00
refls meas	37 407
unique refls	4955
R for merge	0.082
refls in refinement $I > 2.0\sigma(I)$	3102
solution method	Shelxs-97 (Sheldrick, 1990)
parameters refined	399
R_1, wR_2	0.052, 0.121
R_1 for $I > 0.0\sigma(I)$	0.099
GOF	1.04
largest Δ/σ	0.00
final diff map, e $Å^{-3}$	−0.25, +0.39
programs[28]	Shelxl-97 (Sheldrick, 1997)
scattering factors	Internat. Tables for Crystallography, Vol C
H atom treatment	riding

Experimental Section

[9,10,11,12,12a,12f-η^6]-Tricarbonylchromium(0)-2,7-di-*tert*-butyl-*trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene (4). A mixture of benzo[*e*]dimethyldihydropyrene[6] **5** (200 mg, 0.51 mmol), tricarbonylchromiumnaphthalene [27] (200 mg, 0.73 mmol), and dry THF (5 mL, degassed by three freeze−pump−thaw cycles) was placed in a Schlenk tube, equipped with a condenser, under argon. The mixture was then stirred at reflux for 27 h, cooled, and chromatographed on silica gel (Merck 60−200 mesh, deactivated with 5 wt % of concd aq ammonia, column made up, and solvents flushed with argon). Elution with hexane recovered **5** (61 mg, 0.15 mmol). Then elution with hexane/ethyl acetate (1:1) gave the complex **4** as a dark brown solid, 178 mg (0.33 mmol, 64.7%). Recrystallization from hexane yielded dark reddish-purple crystals, mp (some dec) 172−174 °C. ^1H NMR ($CDCl_3$, 360 MHz, spectra available in the Supporting Information, see text for assignments) δ 7.935 (H-8), 7.930 (H-1), 7.197 (H-3), 7.179 (H-6),

(25) Calculated using the PM3 method with PC Spartan Pro; Wavefunction, Inc.: Irvine, CA.
(26) Mitchell, R. H.; Chen, Y. *Tetrahedron Lett.* **1996**, *30*, 5239−5242.
(27) Carroll, D. G.; McGlynn, S. P. *Inorg. Chem.* **1968**, *7*, 1285−1290.
(28) Sheldrick, G. *SHELX-97* A program for crystal structure determination; University of Göttingen: Göttingen, Germany, 1997. Farrugia, L. J. *ORTEP3* for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.

6.940 (H-5), 6.918 (H-4), 6.677 (H-12), 6.602 (H-9), 5.610 (H-10), 5.592 (H-11), 1.43 (s, 18, $-C(CH_3)_3$), −0.825 (s, 3, proximal-CH_3), −1.219 (s, 3, distal-CH_3). Coupling constant data (Hz) by iteration and simulation (see text and Supporting Information; see structure set 1 for H-numbers): $J_{12,11} = 6.96$, $J_{12,10} = 1.12$, $J_{12,9} = 0.13$, $J_{12,1} = 0.75$; $J_{11,10} = 5.85$, $J_{11,9} = 1.12$, $J_{10,9} = 6.95$; $J_{9,8} = 0.75$; $J_{8,6} = 1.35$, $J_{8,1} = -0.85$; $J_{6,5}$ 0.81; $J_{5,4} = 6.37$; $J_{4,3} = 0.83$; $J_{3,1} = 1.34$. ^{13}C NMR ($CDCl_3$, 90.6 MHz; X-ray numbering used C-1,2 means C-1 and C-2; C-1/2 means C-1 or C-2) δ 232.54 (C-1,2,3), 144.50/144.28 (C-12/23), 139.24 (C-18), 138.65 (C-21), 131.74 (C-10), 131.62 (C-29), 121.99/121.92 (C-19/20), 121.48 (C-17), 121.35 (C-22), 121.05 (C-11), 119.46 (C-28), 100.78/100.59 (C-4/9), 90.56 (C-6), 90.11 (C-7), 88.59 (C-8), 86.19 (C-5), 36.29 (C-30), 36.20 (C-32), 35.34/35.24 (C-13/24), 30.31/30.28 (C-14,15,16/25,26,27), 22.39 (C-31, proximal-Me), 17.87 (C-33, distal-Me). IR (KBr, weak unless noted) 2959, 2948, 2921, 2900, 2862, 1973 (s), 1954 (s), 1916 (s), 1892 (s), 1876 (s), 1865 (s), 1620, 1475, 1459, 1443, 1362, 1330, 1260, 1231, 1107, 1045, 884, 819, 801, 674, 658, 637, 626, 612, 529 cm^{-1}; ($CDCl_3$) 1960 (s), 1893 (s,b). UV (cyclohexane) λ_{max}, nm (ϵ_{max}) 313 (25 000), 355 (16 400), 432 (16 600), 560sh (450). CI MS *m/z* 531 (MH^+). HRMS calcd for $C_{33}H_{34}O_3Cr$, 530.1913; found, 530.1911. Anal. Calcd for $C_{33}H_{34}O_3Cr$: C, 74.70; H, 6.46. Found: C, 74.22; H, 6.50.

Crystal Structure. A crystal from the hexane crystallization mentioned previously was selected. The cif file has been submitted in the Supporting Information; only important data are listed in Table 2.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for support of this work.

Supporting Information Available: Copies of the actual and simulated ^1H NMR spectra of **4** and the X-ray cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0269542