Synthesis, Structure, and Reactivity of the *endo*- and *exo*-Tricarbonylchromium Isomers of Dibenzobicyclo[2.2.2]octadiene and Its 2,6-Dimethyl Derivative: X-ray Crystallographic Studies

T. G. Traylor,* Martin J. Goldberg, and Andrew R. Miksztal

Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093

Charles E. Strouse*

Department of Chemistry, University of California, Los Angeles, Los Angeles, California 90024

Received September 8, 1988

The crystal structures of the *endo*- and *exo*-tricarbonylchromium isomers of dibenzobicyclo[2.2.2]octadiene have been determined. The endo isomer displayed negligible distortion, suggesting that its rapid internal and external arene exchange reactions are due to transition-state stabilizations by π-participation rather than ground-state deformations. Crystal data for the endo isomer are as follows: space group $P2_1/n$, a = 7.949 (2) Å, b = 14.338 (4) Å, c = 13.759 (4) Å, β = 101.83 (1)°, V = 1534.9 Å^3; Z = 4. Least-squares refinement on 1963 unique reflections yielded R = 0.066. In contrast, the exo isomer displays deformations, in changes of both Cr–C distances and Cr–C–O bond bending and tilting, consistent with its thermodynamic instability and accounting for its rapid external exchange with arenes. The exo isomer crystals contain two tricarbonyl conformers, affording interesting structural information regarding the nature of steric deformations. Crystal data for the exo isomer are as follows: space group $P2_1/a$, a = 11.885 (3) Å, b = 22.121 (5) Å, c = 12.691 (3) Å, β = 114.86 (1)°, V = 3027.3 Å^3; Z = 8. Least-squares refinement on 3205 unique reflections yielded R = 0.065.

Introduction

In the course of our studies on neighboring group participation of arene exchange reactions of (arene)tricarbonylchromium complexes, the above complexes were synthesized and studied with regard to the mechanism of arene exchange reactions in general.[1,2] The resulting kinetics, described in a previous paper,[3] revealed enhanced internal and external reactivity toward arenes and carbon monoxide and prompted the structural investigations described herein. Previous reports have separately addressed such features as conformational variability in dicarbonyl–phosphine complexes of hexaethylbenzene,[4] sterically induced restricted rotation of arene–metal bonds by bulky alkyl substituents,[5] shifting of the tricarbonylchromium moiety from the arene ring centroid in polyaromatic hydrocarbon complexes,[6] and sterically induced distortions of the hydrocarbon framework in (η^6-triptycene)tetracobaltnonacarbonyl.[7] We have observed all of these features as well as tilting and bending of a metal-bound carbonyl ligand for the *exo*-tricarbonylchromium isomer of dibenzobicyclo[2.2.2]octadiene. The *endo*-tricarbonylchromium isomer, on the other hand, resembles many other alkyl(arene)tricarbonylchromium complexes[8] and (triptycene)tricarbonylchromium, whose crystal structure has recently been determined.[7] Along with this is the isolation of a (1,2-dialkylarene)tricarbonylchromium complex with a conformation having a metal-bound carbonyl ligand bisecting the 1,2 carbon–carbon bond. In answering the original objective of this work, the data offer insight into the source of the increased intra- and intermolecular reactivity observed for these interesting yet simple (arene)tricarbonylchromium complexes.

Experimental Section

General Data. ^{1}H NMR spectra were taken on a constructed spectrometer using Nicolet software, operating at 360 MHz. ^{13}C NMR were acquired on a Jeol X-100 spectrometer operating at 25 MHz using 7500–32 000 acquisitions.

Chromium Complexes. The synthesis and separation of the *endo*- and *exo*-tricarbonylchromium isomers of dibenzobicyclo[2.2.2]octadiene has been described elsewhere.[3]

Crystallography. Single crystals of each isomer, suitable for X-ray analysis, were grown by layering a saturated solution of the complex in ethyl acetate with a 10-fold volume of hexanes and allowing the solutions to diffuse over a period of 20–40 h in the dark at room temperature. The solvent mixture was decanted off, and crystals were dried by using a gentle stream of argon. Intensity data were measured on a Picker diffractometer. Crystal and data collection parameters are given in Tables II and III. All data analysis made use of the University of California, Los Angeles Crystallographic Computing Package.

A suitable crystal of either the *exo*- or *endo*-$Cr(CO)_3$ isomer was covered with fast drying epoxy cement and mounted on the diffractometer. The cell constants and orientation matrix were determined from a least-squares fit after 20 reflections. Of a total of 3134 and 5933 reflections collected for the endo and exo isomers, respectively, including those systematically absent, 1963 and 3205 reflections had $I > 3\sigma(I)$ and were used to solve and refine the endo and exo structures, respectively. No absorption corrections

---

[1] Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445.

[2] Traylor, T. G.; Goldberg, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 3968.

[3] Traylor, T. G.; Goldberg, M. J. *Organometallics* **1987**, *6*, 2413.

[4] Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448.

[5] Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 661.

[6] (a) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* **1967**, *50*, 1052. (b) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, 467. (c) Dueschl, H.; Hoppe, W. *Acta Crystallogr.* **1964**, *17*, 800. (d) Hanic, F.; Mills, O. S. *J. Organomet. Chem.* **1968**, *11*, 151. (e) Pettersen, R. C.; Cullen, D. L.; Pearce, H. L.; Shapiro, M. J.; Shapiro, B. L. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2360. (f) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 264.

[7] Gancarz, R. A.; Blount, J. F.; Mislow, K. *Organometallics* **1985**, *4*, 2028.

[8] (a) Sneeden, R. P. A. *Organochromium Complexes*; Academic Press: New York, 1975; pp 116–120 and references therein. (b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499.

0276-7333/89/2308-1101$01.50/0

Table I. Spectroscopic Data for Dibenzobicyclo[2.2.2]octadiene (1) and Its *endo*- and *exo*-Tricarbonylchromium Complexes (2 and 3, Respectively)

	^{13}C NMR^a								
compd	C1,6	C2,5	C3,4	C7,14	C8,13	C9,12	C10,11	C15,16	C_{CO}
1				43.9	143.6	125.4	123.1	26.6	
2	114.6	91.0	89.8	42.0	141.8	126.6	123.0	26.8	234.6
3	121.1	91.0	90.0	42.4	142.8	126.5	123.7	29.3	233.1

	^{1}H NMR (δ)^a						
compd	H2,5	H3,4	H7,14	H9,12	H10,11	H15,16^b	H15,16^c
1			4.07	7.04	7.03	1.49	1.49
2	4.83	4.48	3.41	7.12	7.12	1.07	1.23
3	4.71	4.24	3.29	6.92	6.90	2.04	1.24

[a] Chemical shifts are in parts per million. [b] Methylene protons syn to the complexed ring. [c] Methylene protons anti to the complexed ring.

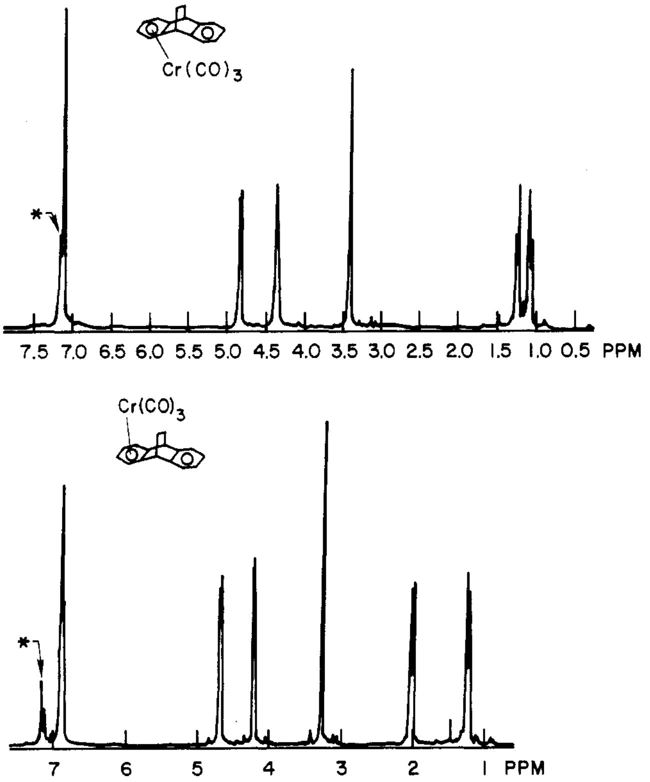


Figure 1. ^{1}H NMR (360 MHz) spectra of the *endo*- and *exo*-$Cr(CO)_3$ isomers of dibenzobicyclo[2.2.2]octadiene in benzene-d_6 at 28 °C.

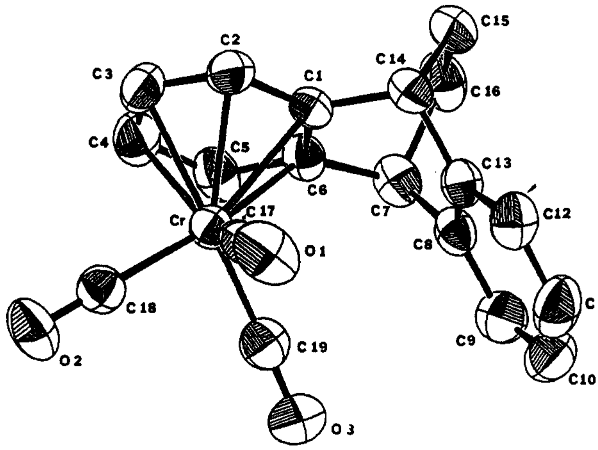


Figure 2. ORTEP diagram showing the numbering scheme for *endo*-$Cr(CO)_3$-dibenzobicyclo[2.2.2]octadiene. All hydrogen atoms have been excluded for clarity.

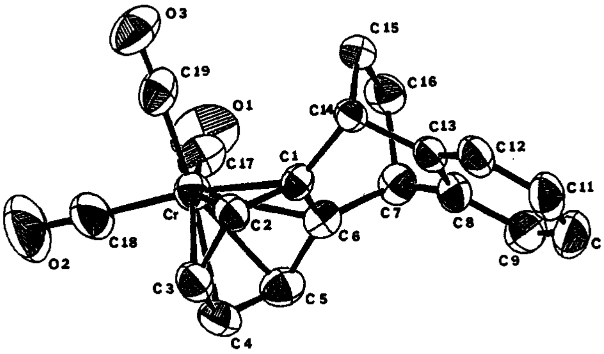


Figure 3. ORTEP diagram showing the numbering scheme for *exo*-$Cr(CO)_3$-dibenzobicyclo[2.2.2]octadiene (structure A). All hydrogen atoms have been excluded for clarity.

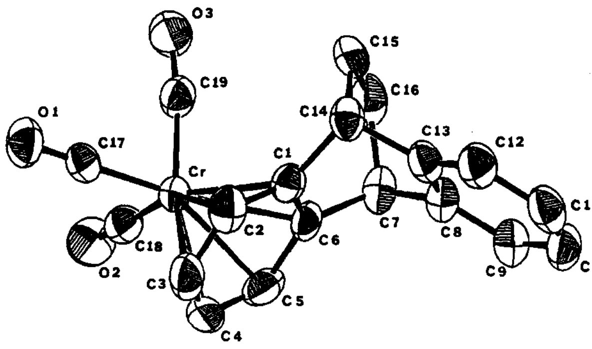


Figure 4. ORTEP diagram showing the numbering scheme for *exo*-$Cr(CO)_3$-dibenzobicyclo[2.2.2]octadiene (structure B). All hydrogen atoms have been excluded for clarity.

were applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. Calculated H atom positions (C–H = 1.0 Å) were used in structure factor calculations. The final least-squares refinement led to weighted R values and errors of fit listed in Tables II and III as well as data to refined parameter ratios of 9.4 and 7.7 for the *endo*- and *exo*-$Cr(CO)_3$ isomers, respectively. The last difference map was featureless (i.e. peak intensities less than 0.10 e/Å^3 for the endo isomer and 0.94 e/Å^3 for the exo). Detailed data are filed as supplementary material.

Results

The *exo*- and *endo*-tricarbonylchromium complexes of dibenzobicyclo[2.2.2]octadiene were prepared via reaction of the free hydrocarbon, with hexacarbonylchromium followed by separation of the isomers by chromatography on silica gel, as described elsewhere.[3] Spectroscopic data for the two isomers is given in Table I, along with that for the free hydrocarbon. Peak assignments for both ^{13}C and ^{1}H NMR data were made by various decoupling procedures and, where possible, comparison with known structures such as *o*-xylene, (*o*-xylene)tricarbonylchromium, and the exo isomer itself along with its *anti*-15,16-dideuterio analogue[9]. ^{1}H NMR spectra of the endo and exo isomers are shown in Figure 1. Numbering system used for all atoms is the same for both isomers and shown

Table II. Crystal and Data Collection Parameters for *endo*-Cr(CO)$_3$-Dibenzobicyclo[2.2.2]octadiene

mol formula	$CrC_{19}H_{14}O_3$
space group	$P2_1/n$
a, Å	7.949 (2)
b, Å	14.338 (4)
c, Å	13.759 (4)
β, deg	101.83 (1)
MW	342.3
V, Å^3	1534.9
Z	4
color	yellow
habit	multifaceted parallelpiped
temp, K	298
radiatn	Mo Kα (λ = 0.71070 A)
scan type	θ–2θ
scan speed, deg/min	18.0
cryst dimens, mm	0.3 × 0.3 × 0.2
data collected	$+h,+k,\pm l$ for $2\theta < 50°$; 3134 reflections
range of h,k,l	0,0,4 to 9,5,−3
error of fit	2.04
R	0.051
R_w	0.066

Table III. Crystal and Data Collection Parameters for *exo*-Cr(CO)$_3$-Dibenzobicyclo[2.2.2]octadiene

mol formula	$CrC_{19}H_{14}O_3$
space group	$P2_1/a$
a, Å	11.885 (3)
b, Å	22.121 (5)
c, Å	12.691 (3)
β, deg	114.86 (1)
MW	342.3
V, Å^3	3027.3
Z	8
color	yellow
habit	rectangular parallelpiped
temp, K	298
radiatn	Mo Kα (λ = 0.71070 A)
scan type	θ–2θ
scan speed, deg/min	6.0
cryst dimens, mm	0.2 × 0.2 × 0.15
data collected	$+h,+k,\pm l$ for $2\theta < 50°$; 5933 reflctns
range of h,k,l	0,0,1 to 14,3,−7
error of fit	1.74
R	0.055
R_w	0.065

in Figure 2–4. Complexation of the arene by Cr(CO)$_3$ results in the usual upfield shift of the aromatic protons by 2–3 ppm as well as splitting into an A_2B_2 pattern. A smaller upfield shift is seen for the methine protons ($\Delta\delta$ = 0.6–0.7 ppm), in line with that seen for other alkyl protons α to a complexed arene ring. The most significant difference between the two isomers is the shifts of the methylene protons, split from a singlet in the free hydrocarbon to an A_2B_2 pattern for both isomers, with those protons syn to the Cr(CO)$_3$ group in the exo isomer deshielded by approximately 1 ppm. This shift is also observable in the ^{13}C NMR where the methylene carbons C(15,16) are shifted downfield by 2–3 ppm in the exo isomer (29.3 ppm) relative to the endo isomer (26.8 ppm) and free hydrocarbon (26.6 ppm). The most significant difference between the two isomers in the ^{13}C NMR is the shift of the quartenary carbons C(1,6) of the complexed ring which are shifted 7 ppm downfield in the exo (121.1 ppm) relative to the endo (114.6 ppm) isomer. Both complexes exhibit a single ^{13}C peak for the metal-bound carbonyl ligands. The uncomplexed portion of both compounds correspond well with similar shifts in the parent hydrocarbon, also given in Table I.

Crystal data for the two isomers are given in Tables II–V and will be discussed separately in detail below.

Table IV. Selected Bond Lengths[a] and Angles[b] for *endo*-Cr(CO)$_3$-Dibenzobicyclo[2.2.2]octadiene

Cr–C(17)	1.820 (5)	O(1)–C(17)	1.159 (5)
Cr–C(18)	1.839 (5)	O(2)–C(18)	1.153 (5)
Cr–C(19)	1.839 (5)	O(3)–C(19)	1.165 (5)
Cr–C(1)	2.245 (4)	C(1)–C(6)	1.404 (6)
Cr–C(2)	2.225 (4)	C(2)–C(3)	1.412 (6)
Cr–C(3)	2.212 (4)	C(4)–C(5)	1.394 (6)
Cr–C(4)	2.214 (4)	C(8)–C(13)	1.395 (5)
Cr–C(5)	2.235 (4)	C(9)–C(10)	1.391 (7)
Cr–C(6)	2.250 (4)	C(11)–C(12)	1.372 (6)

C(17)–Cr–C(18)	89.4 (2)	C(16)–C(7)–C(8)	107.3 (3)
C(17)–Cr–C(19)	87.7 (2)	C(13)–C(8)–C(9)	119.9 (4)
C(18)–Cr–C(19)	87.7 (2)	C(8)–C(9)–C(10)	118.8 (4)
Cr–C(17)–O(1)	179.2 (4)	C(9)–C(10)–C(11)	120.9 (5)
Cr–C(18)–O(2)	179.3 (4)	C(10)–C(11)–C(12)	120.2 (5)
Cr–C(19)–O(3)	177.6 (4)	C(11)–C(12)–C(13)	120.1 (4)
C(2)–C(1)–C(6)	119.5 (4)	C(12)–C(13)–C(8)	119.9 (4)
C(2)–C(3)–C(4)	120.0 (4)	C(13)–C(14)–C(15)	106.5 (3)
C(4)–C(5)–C(6)	118.3 (4)	C(13)–C(14)–C(1)	108.6 (3)
C(6)–C(7)–C(8)	108.7 (3)	C(1)–C(14)–C(15)	105.0 (3)
C(6)–C(7)–C(16)	103.8 (4)		

[a] In angstrom units. Standard deviations in parentheses. [b] In degrees. Standard deviations in parentheses.

Table V. Selected Bond Lengths[a] and Angles[b] for *exo*-Cr(CO)$_3$-Dibenzobicyclo[2.2.2]octadiene

	A	B
Cr–C(17)	1.815 (6)	1.810 (6)
Cr–C(18)	1.821 (7)	1.829 (6)
Cr–C(19)	1.825 (7)	1.814 (6)
Cr–C(1)	2.258 (5)	2.272 (5)
Cr–C(2)	2.216 (6)	2.236 (6)
Cr–C(3)	2.211 (6)	2.191 (6)
Cr–C(4)	2.212 (6)	2.201 (6)
Cr–C(5)	2.225 (6)	2.212 (6)
Cr–C(6)	2.265 (5)	2.281 (5)
O(1)–C(17)	1.162 (7)	1.159 (6)
O(2)–C(18)	1.158 (7)	1.148 (7)
O(3)–C(19)	1.151 (7)	1.164 (6)
C(1)–C(6)	1.405 (6)	1.401 (7)
C(2)–C(3)	1.396 (7)	1.407 (9)
C(4)–C(5)	1.401 (8)	1.405 (9)
C(8)–C(13)	1.397 (7)	1.385 (7)
C(9)–C(10)	1.382 (8)	1.385 (8)
C(11)–C(12)	1.386 (8)	1.400 (9)
C(17)–Cr–C(18)	87.7 (3)	89.1 (2)
C(17)–Cr–C(19)	88.4 (3)	85.9 (2)
C(18)–Cr–C(19)	87.6 (3)	85.6 (3)
Cr–C(17)–O(1)	177.6 (6)	178.9 (5)
Cr–C(18)–O(2)	177.4 (7)	178.6 (6)
Cr–C(19)–O(3)	178.5 (6)	172.5 (5)
C(2)–C(1)–C(6)	120.2 (5)	121.8 (6)
C(2)–C(3)–C(4)	120.3 (5)	120.9 (6)
C(4)–C(5)–C(6)	119.2 (5)	119.4 (6)
C(6)–C(7)–C(8)	105.1 (4)	103.6 (5)
C(6)–C(7)–C(16)	109.2 (5)	109.0 (5)
C(16)–C(7)–C(8)	107.3 (5)	107.5 (5)
C(13)–C(8)–C(9)	119.1 (6)	119.9 (6)
C(8)–C(9)–C(10)	120.1 (6)	120.2 (6)
C(9)–C(10)–C(11)	120.7 (5)	120.1 (6)
C(10)–C(11)–C(12)	119.6 (6)	120.8 (6)
C(11)–C(12)–C(13)	120.0 (6)	118.0 (6)
C(12)–C(13)–C(8)	120.6 (5)	120.2 (6)
C(13)–C(14)–C(15)	106.4 (4)	106.3 (5)
C(13)–C(14)–C(1)	104.5 (4)	103.9 (5)
C(1)–C(14)–C(15)	109.6 (4)	108.6 (5)

[a] In angstrom units. Standard deviations in parentheses. [b] In degrees. Standard deviations in parentheses.

Discussion

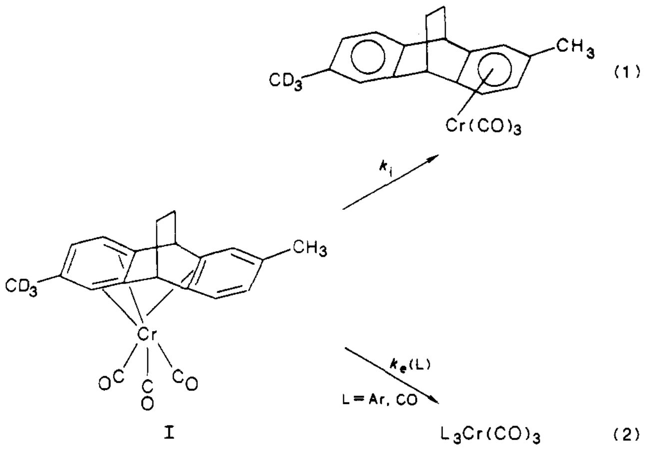
***endo*-Cr(CO)$_3$ Isomer of Dibenzobicyclo[2.2.2]octadiene.** First we turn our discussion to the structure of the endo isomer, shown in Figure 2. The positional parameters for all non-hydrogen atoms are listed in Table

---

(9) Trahanovsky, W. S.; Baumann, C. R. *J. Org. Chem.* **1974**, *39*, 1924.

II. Selected bond lengths and interatomic angles (Table IV) resemble those for many other alkyl substituted (arene)tricarbonylchromium complexes including the closely related (triptycene)tricarbonylchromium.[7] The Cr–C_{Ar} bond distances average to a normal 2.230 (4) Å with the longest distances being to the quartenary carbons (2.245 (4) and 2.250 (4) Å for Cr–C(1) and Cr–C(6), respectively). Similar to all other ortho disubstituted complexes, the carbonyl ligands bisect the C(1)–C(2), C(3)–C(4), and C(5)–C(6) bonds.[8] The average C_{Ar}–C_{Ar} bond distance for the complexed ring, 1.406 (6) Å, is slightly longer than that for the uncomplexed ring, 1.386 (6) Å, properties analogous to other (arene)tricarbonylchromium complexes.[6,7] The average bond lengths (1.833 (5) Å for Cr–C_{CO}, 1.159 (5) for Å for C–O) and angles (88.3 (2)° for C_{CO}–Cr–C_{CO}, 178.7 (4)° for Cr–C–O) associated with the carbonyl ligands are those expected by comparison with known structures.[8a] Both arene rings are within 2° of regular hexagons and essentially planar, with the maximum deviation of 0.012 Å from the least-squares plane defined by all six atoms. The usual trend in 1,2-disubstituted arene complexes for bowing about the 3,6-carbons[10] is observed here. The angles about C(13)–C(14)–C(1), 108.6 (3)°, and C(6)–C(7)–C(8), 108.7 (3)°, are within experimental error of those found for the adducts of anthracene with tetracyanoethylene[11] and anthracene with maleic anhydride[12] and indicate no nonbonding interactions between the $Cr(CO)_3$ group and the uncomplexed ring. This is further substantiated by ^{13}C NMR data in which the C(13) and C(8) carbons are actually shifted upfield in the complex relative to the free hydrocarbon, opposite from the downfield shift observed for the methylene bridge carbons C(15) and C(16) (and protons) of the exo isomer in which significant through-space interaction does occur. The observation of a single peak for the metal-bound carbonyl ligands in the ^{13}C NMR at 234.6 ppm also precludes any severe interactions between the $Cr(CO)_3$ and uncomplexed ring which would lead to a loss in equivalency of these carbon atoms as a result of restricted rotation about the arene–metal bond. Instead, this result is in accord with previous studies which found the barrier to rotation about the arene–metal bond to be as low as 1–3 kcal/mol.[13]

In relating the crystal structure to the kinetics discussed in the previous paper,[3] one need recall that the endo isomer showed rapid internal arene exchange as well as accelerated reaction with benzene and carbon monoxide above that predicted on thermodynamic grounds. The distance from the chromium atom to the C(8)–C(13) bond is 3.67 Å, only 0.5 Å greater than the combined van der Waals radii of chromium and carbon. This short distance, combined with the conformational ridgity (i.e. no rotation about the arene–methine carbon–carbon bond) of the molecule, suggests that only a slight shift of the $Cr(CO)_3$ group could achieve a structure of the type shown below (I), which can lead to rapid internal arene exchange or "catalysis" of external attack by arenes or carbon monoxide (eq 1 and 2).



***exo*-$Cr(CO)_3$ Isomers of Dibenzobicyclo[2.2.2]octadiene.** The exo isomer, which was crystallized under conditions identical with the endo isomer, revealed a unit cell containing two distinct structures, labeled A and B, shown in Figures 3 and 4, respectively. Selected bond lengths and angles for A and B are listed in Table V. The most obvious difference between the two molecules is the conformation of the tricarbonylchromium unit. In A, the carbonyl ligands adopt the normal geometry, bisecting the arene C(1)–C(2), C(3)–C(4), and C(5)–C(6) bonds (Figure 3). In B, however, the $Cr(CO)_3$ tripod has been rotated 60° about the chromium–arene bond, and the carbonyls now bisect the C(1)–C(6), C(2)–C(3), and C(4)–C(5) bonds (Figure 4). This constitutes the first isolated ortho-disubstituted (arene)$Cr(CO)_3$ complex with a carbonyl ligand bisecting the quartenary carbon–carbon bond. The only similar example where the $Cr(CO)_3$ moiety adopts such an orientation is in (biphenylene)$Cr(CO)_3$.[8b] Here the conformational change has been explained in terms of attractive and repulsive electronic interactions between the $Cr(CO)_3$ hybrid orbitals and the π-system of the uncomplexed ring.[14] Clearly, this effect cannot be operative in the dibenzobicyclo[2.2.2]octadiene ligand where there is no π-orbital mixing of the aromatic systems, based upon aromatic nitration of this and related dibenzobicyclic compounds.[15] Crystal structures of A and B also show several deformations in the dibenzobicyclic ligand itself, which probably adds to the inherent instability and thus enhanced external arene exchange of the exo versus endo isomer in benzene (254×10^{-7} s^{-1} and 58×10^{-7} s^{-1}, respectively).

First, there is a bowing of the hydrocarbon ligand about the methine carbons in the exo isomer. In the *endo*-$Cr(CO)_3$ complex the C(1)–C(13) and C(6)–C(8) distances are equal, within experimental error at 2.449 (4) and 2.452 (4) Å, respectively. On going to A, the C(1)–C(13) distance is the longer of the two at 2.398 (4) Å with C(6)–C(8) now being 2.391 (4) Å. For B, the difference of the distance between the atom pairs is the largest of all three structures, being 2.383 (4) and 2.368 (4) Å for C(1)–C(13) and C(6)–C(8), respectively. Though these changes are small and, with the exception of B, all within experimental error, the trend is notable. The overall shortening of these distances from an average of 2.45 Å in the endo isomer to 2.40 Å for A and 2.38 Å for B might be due to steric repulsion between the $Cr(CO)_3$ moiety and the syn methylene hydrogens, discussed further below.

---

(10) Mills, O. S. *Pure Appl. Chem.* **1969**, *20*, 117.

(11) Karle, I. L.; Fratini, A. V. *Acta Crystallogr., Sect. B* **1970**, *B26*, 596.

(12) Bulgarovskii, I. V.; Zvonkovam, Z. V.; Il'ina, I. G. *J. Struct. Chem. (Engl. Transl.)* **1979**, *20*, 755.

(13) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546 and references therein. (b) Chiu, N. S.; Schafer, L.; Seip, R. *J. Organomet. Chem.* **1975**, *101*, 331. (c) Evidence put forth in ref 8b indicates a barrier to rotation of 1–3 kcal/mol. (d) Randall, E. W.; Rosenberg, E.; Milone, L. *J. Chem. Soc., Dalton Trans.* **1973**, 1672.

(14) Shakir, R.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D., unpublished results.

(15) Klanderman, B. H.; Perkins, W. C. *J. Org. Chem.* **1969**, *34*, 630. Recent gas-phase PE studies of triptycene have concluded that through-space mixing does occur for the six highest occupied π-MO's, in contradiction with the solution work discussed in the text, see: Kobayashi, T.; Kubota, T.; Ezumi, K. *J. Am. Chem. Soc.* **1983**, *105*, 2172.

The second deformation of the ligand involves changes in the angles between the three planes defined by atoms C(7)-C(6)-C(1)-C(14), C(7)-C(8)-C(13)-C(14), and C(7)-C(16)-C(15)-C(14), labeled ϕ_1, ϕ_2, and ϕ_3, respectively. Examination of the angles about C(7) and C(14) show that the introduction of steric interactions for A and B causes folding of the hydrocarbon only on that side of the molecule where the $Cr(CO)_3$ is bound. The average value of the C(8)-C(7)-C(16) and C(13)-C(14)-C(15) bond angles is the same, 106.0 (3)°, in the endo isomer and both A and B. However, the other two sets of angles about the methine carbons are different among the isomers. The average of C(6)-C(7)-C(16) and C(1)-C(14)-C(15) bond angles has increased from 104.4 (4)° in the endo complex to 109.4 (5)° in A to 108.8 (5)° in B. Concomitant with this opening is a closure of the C(6)-C(7)-C(8) and C(1)-C(14)-C(13) bond angles from an average of 108.7 (3)° in the endo isomer to 104.8 (4)° in A and even further to 103.8 (5)° in B.

The dihedral angles between the least-squares planes containing the methine carbon atoms (C(7) and C(14)) with the quartenary carbon atoms of both phenyl rings (C(1)-C(6) and C(8)-C(13)) and methylene bridge (C(15)-C(16)) atoms also reflects this "opening" in the side of the molecules where the $Cr(CO)_3$ group is bound, deviating from essentially 120° between all three planes in the endo isomer to 122°, 118°, and 120° for ϕ_1, ϕ_2, and ϕ_3 respectively, in both A and B. Also observed for A and B is a further bending of the complexed aromatic ring away from the methylene bridge by dihedral angles of 7° and 9°, respectively, between the arene least-squares plane and plane containing atoms C(7)-C(6)-C(1)-C(14). The complexed ring of the endo isomer, on the other hand, is bent in the opposite direction by approximately 2-3°. In all three complexes the uncomplexed ring is essentially planar with respect to atoms C(7)-C(8)-C(13)-C(14). All distortions of the hydrocarbon framework that occur upon going from endo to exo bonding of the $Cr(CO)_3$ group are virtually identical with those seen by Mislow and coworkers for the complexation of triptycene by a $Cr(CO)_3$ group and the bulky $Co_4(CO)_9$ cluster, respectively.[7]

The third result of the repulsion of the carbonyl group and methylene hydrogens is both a bending and tilting of the carbonyl ligand in B. The lengths of the $Cr-C_{CO}$ and C-O bonds, 1.818 (6) and 1.157 (6) Å, respectively, are unchanged from their normal values, observed in virtually all (arene)tricarbonylchromium complexes.[8a] However, the $C_{CO}-Cr-C_{CO}$ and $Cr-C_{CO}-O$ bond angles, which have typical average values of 88.3 (2)°, 187.7 (4)°, and 87.9 (3)°, 177.8 (6)° for the endo and exo A compounds, respectively, have both been distorted in B. Here the C(19)-Cr-C(17) and C(19)-Cr-C(18) angles have been decreased by approximately 4° to 85.9 (2)° and 85.6 (3)°, respectively, while the C(17)-Cr-C(18) bond angle has a value of 89.1 (2)°, opened up slightly to compensate for the other two. Along with this tilting of the carbonyl ligand, is a 6° bending of the C-O bond from 178.9 (5)° for Cr-C(17)-O(1) and 178.6 (6)° for Cr-C(18)-O(2) (values similar to those in the endo isomer and A) to 172.5 (5)° for Cr-C(19)-O(3). The steric deformation of the Fe-C-O bond in heme proteins continues to be discussed in terms of either a bending or tilting of the carbonyl group, but the data do not allow a definite decision concerning the contributions of each.[16] Our results indicate that the carbonyl group responds to steric interactions by both bending about 6° and tilting 4°. Since the distance O(3)-C(15,16) is 3.5 Å and that of C(19)-C(15,16) is 3.3 Å, tilting is expected. Thus in heme proteins, where the steric interaction is with oxygen, bending should dominate the effect.

The fourth, and perhaps most interesting, feature resulting from steric interactions operative in the exo isomers is a lengthening of the $Cr-C_{Ar}$ bonds to the quartenary carbons. For all three complexes the average $Cr-C_{Ar}$ bond distance is 2.23 (5) Å, which is the same value found for all (arene)tricarbonylchromium compounds, monoaromatic and polyaromatic alike.[8a] However, the differene between the longest (Cr-C(1) or Cr-C(6)) and shortest (Cr-C(3) or Cr-C(4)) of these bonds changes drastically. Going from endo to A to B, the differences increase from 0.04 to 0.05 Å and up to 0.09 Å, respectively. The *exo*-$Cr(CO)_3$ adducts of *exo*-2-acetoxybenzonorbornene[17] and triptycene[7] both show differences of 0.04 Å, similar to the endo isomer reported here. Only upon π-bonding of a $Co_4(CO)_9$ ligand to triptycene does the observed difference equal that of B. The shift of 0.09 Å for B is the largest value of its kind for all alkyl-substituted (arene)tricarbonylchromium complexes whose structures have been determined and is on the order observed for π-complexes of polyaromatic hydrocarbons such as naphthalene (0.15 Å),[6a] anthracene (0.13 Å),[6d] and phenanthrene (0.08 Å).[6b,c] In these cases, the lengthening has been ascribed to the ring juncture carbons being π-bonded to three other carbon atoms and thus less available for π-interactions with the chromium atom[18] and/or as a consequence of maintaining maximum aromaticity in the uncomplexed ring.[8b] Obviously, neither of these effects can be operative in the present system. Steric interactions have been invoked to explain large (0.09 Å) $Cr-C_{Ar}$ bond length differences observed for (triptycene)$Co_4(CO)_9$[7] and (hexaethylbenzene)$Cr(CO)_2P(Ph)_3$.[4]

The enhanced $Cr-C_{Ar}$ bond length differences of A and B over that for the endo isomer is also observable in the ^{13}C NMR. As seen in Table I, the only difference in the spectra of the two isomers is the shift of C(1) and C(6) carbons, which appear 7 ppm downfield for the exo isomer relative to the endo. Reduced bonding of chromium to these carbon atoms would cause such a shift to lower field where the uncomplexed aromatic carbons in both isomers and the free hydrocarbon appear.

In conclusion, we have given firm structural data to compliment our earlier kinetic studies which deduced that the key intermediate in arene exchange reactions involves diene-like and olefin-like bonding of the two phenyl groups simultaneously to a single tricarbonylchromium group. This intermediate, if stabilized enough, can lead to the use of an arene to "catalyze" attack of nucleophiles at the metal. Furthermore, the many interesting effects discussed here, all of which arise from simple oxygen-hydrogen repulsions, are probably responsible for the thermal instability and thus high external arene exchange reactivity observed for *exo*-$Cr(CO)_3$-dibenzobicyclo[2.2.2]octadiene, discussed in detail in the preceding paper.[3]

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE 81-20969, for support of this research.

Supplementary Material Available: Tables of spectroscopic data (Table I), crystal data (Tables II and III), final coordinates (Tables IV and VII), bond lengths (Tables V, VIII, and X), and bond angles (Tables VI, IX, and XI) (12 pages). Ordering information is given on any current masthead page.

---

(16) (a) Baldwin, J. *J. Mol. Biol.* **1980**, *136*, 103. (b) Baldwin, J.; Clothia, C. *J. Mol. Biol.* **1979**, *129*, 175.

(17) Taylor, I. F., Jr.; Griffith, E. A. H.; Emma, E. L. *Acta Crystallogr., Sect. B* **1976**, *B32*, 653.

(18) (a) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1866. (b) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, 467.