magnitude 1.30 and 1.60 or greater for compounds IIIa and IIIb, respectively. An E map based on the set of phases for the solution with a consistency index of 0.950 (second highest) and 0.999 (highest) for IIIa and IIIb, respectively, gave a partial solution for each structure. Successive Fourier syntheses revealed the remaining non-H atom locations. Anisotropic least-squares refinement of all non-hydrogen atoms resulted in final atom locations for which the largest parameter shift was less than 10% of its standard deviation. Final positional parameters with estimated standard deviations are given in Tables IX and X. Hydrogen atoms were included at calculated positions with C–H bond distances of 0.95 Å. Hydrogen atom positions were recalculated after each cycle of least-squares refinement and assigned isotropic thermal parameters equal to the equivalent B (Å^2) of the carbon to which it is bonded. Scattering factors for the neutral atoms were taken from ref 37: those for silicon, germanium, and tin were corrected for anomalous dispersion. Maximum residual electron densities in the final electron difference map for IIIa and IIIb were 0.30 and 0.99 e/Å^3, respectively.

During the refinement of IIIa a disorder of the silicon and germanium atoms was identified. Refinement of the occupancy factors for Ge and Si revealed a 50/50 disorder for these atoms; the refinement was completed by using an average Si–Ge scattering factor curve.

Acknowledgment. W.Z.M. is grateful for partial support of this research by The Graduate School of the University of Missouri—St. Louis.

Registry No. (E)-IIa, 87938-51-0; (Z)-IIa, 87938-61-2; IIb, 87938-52-1; IIc, 33022-24-1; IId, 87938-53-2; IIe, 87938-54-3; IIIa, 87938-55-4; IIIb, 87938-56-5; IIIc, 87938-57-6; Va, 87938-58-7; Vb, 75302-84-0; VIa, 87938-59-8; VIb, 87938-60-1; $MeHSiCl_2$, 75-54-7; Ph_2SiMe_2, 778-24-5; $MePh_2SiH$, 776-76-1; MeLi, 917-54-4; Me_2GeCl_2, 1529-48-2; Ph_2PbCl_2, 2117-69-3; Me_2SiCl_2, 75-78-5; $MePhSiCl_2$, 149-74-6; Me_2SnCl_2, 753-73-1; NBS, 128-08-5; *o*-dibromobenzene, 583-53-9; *o*-chlorobromobenzene, 694-80-4; 5-methyl-5*H*-dibenzosilole, 53268-89-6; *o,o'*-dibromobiphenyl, 13029-09-9; 5,5-dimethyldibenzosilole, 13688-68-1; methylchlorosilane, 993-00-0.

Supplementary Material Available: Tables of hydrogen atom coordinates and thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, least-squares planes, molecular drawings with anisotropic thermal ellipsoids, and structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

---

(37) "International Tables for X-ray Crystallography"; Henry, N. F. M., Lonsdale, L., Eds.; Kynoch Press: Birmingham, England, 1952; Vol. 1.

Structure of (Biphenylene)- and (Triphenylene)Cr(CO)$_3$. An Analysis of the Bonding of Cr(CO)$_3$ to Bicyclic Polyenes

Robin D. Rogers,[1a] Jerry L. Atwood,*[1b] Thomas A. Albright,*[1c,e] William A. Lee,[1d] and
Marvin D. Rausch*[1d]

Departments of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, University of Alabama, University, Alabama 35486, University of Houston, Houston, Texas 77004, and University of Massachusetts, Amherst, Massachusetts 01003

Received August 30, 1983

The preparation and description of the molecular structure of (biphenylene)Cr(CO)$_3$, **1**, and (triphenylene)Cr(CO)$_3$, **2**, are given. The crystal data are as follows: (1) a = 7.065 (4) Å, b = 11.066 (5) Å, c = 8.030 (4) Å, β = 98.43 (3)°, Z = 2, space group $P2_1/m$; (2) a = 12.994 (5) Å, b = 14.766 (5) Å, c = 9.393 (4) Å, β = 121.63 (3)°, Z = 4, space group $C2/m$. The structures were refined to R_w values of 0.033 and 0.027 for **1** and **2**, respectively. The bond localization in biphenylene is somewhat reduced in the Cr(CO)$_3$ complex. While the conformations of the Cr(CO)$_3$ group in **2** and all other polynuclear (benzenoid)Cr(CO)$_3$ complexes have the symmetry unique carbonyl ligand pointed away from the uncoordinated portion of the polyene, the conformation for **1** is reversed. Molecular orbital calculations at the extended Hückel level were carried out to establish the bonding in **1** and the related (naphthalene)Cr(CO)$_3$. A rationale is given for this conformational preference, and a general theoretical strategy is developed to predict the favored conformation in any bicyclic (polyene)ML$_3$ complex.

Introduction

Polycyclic hydrocarbons have fascinated organic chemists for many years with their preparation and physical properties.[2] Naturally, this has been extended to the transition-metal complexes of these compounds.[3] Of particular interest has been the ability of transition metals to stabilize antiaromatic polyenes, with cyclobutadiene[4] being the prime example. Structurally, while singlet cyclobutadiene is probably rectangular,[5] the Fe(CO)$_3$ complexes among others are square.[6] Biphenylene[7] is another well-known example which in the ligand itself shows bond localization as deduced from X-ray[8a,b] and electron dif-

---

(1) (a) Northern Illinois University. (b) University of Alabama. (c) University of Houston. (d) University of Massachusetts. (e) Camille and Henry Dreyfus Teach-Scholar, 1980–1984; Alfred P. Sloan Research Fellow, 1982–1984.

(2) (a) "Nonbenzenoid Aromatics", Snyder, J. P., Ed.; Academic Press: New York, 1969. (b) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964. (c) "Cyclobutadiene and Related Compounds"; Cava, M. P., Mitchell, M. J., Eds.; Academic Press: New York, 1967.

(3) (a) Zeiss, H. H.; Wheatley, P. J.; Winkler, H. J. S. "Benzenoid-Metal Complexes"; Ronald Press: New York, 1966. (b) Deganello, G. "Transition Metal Complexes of Cyclic Polyolefins"; Academic Press: New York, 1979. (c) Tsutsui, M.; Levy, M. N.; Nakamura, A.; Ichikawa, M.; Mori, K. "Introduction to Metal-π Complex Chemistry"; Plenum Press: New York, 1970. (d) Coates, G. E.; Green, M. L. H.; Powell, P.; Wade, K. "Principles of Organometallic Chemistry"; Halsted Press: New York, 1971. (e) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47.

(4) Efraty, E. *Chem. Rev.* **1977**, *77*, 691. Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1.

(5) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4274. Masamune, S.; Souto-Bachille, F. A.; Machiguchi, T.; Bertie, J. E. *Ibid.* **1978**, *100*, 4889.

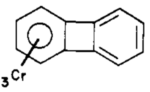
(6) For a review of these structures see: Davis, R. E.; Riley, P. E. *Inorg. Chem.* **1980**, *19*, 674.

(7) For a review of the chemical, physical, and theoretical properties see; Barton, J. W. In "Nonbenzenoid Aromatics"; Synder, J. P., Ed.; Academic Press: New York, 1969; Vol. 1, Chapter 2.

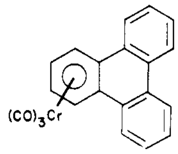
(8) (a) Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* **1966**, *20*, 87. (b) Mak, T. C. W.; Trotter, J. *J. Chem. Soc.* **1962**, 1. (c) Yokozeki, A.; Wilcox, C. F., Jr.; Bauer, S. H. *J. Am. Chem. Soc.* **1974**, *96*, 1026.

0276-7333/84/2303-0263$01.50/0

fraction[8c] studies. It is, therefore, of interest how much a ML_n complex of biphenylene will modify its structure. Chatt and co-workers[9] prepared a bis $Mo(CO)_3$ complex of biphenylene. This paper reports the $Cr(CO)_3$ complex, 1, and its structure. Additionally we have prepared and structurally categorized (triphenylene)$Cr(CO)_3$, 2, to probe not only its geometrical relationship to 1 but also $Cr(CO)_3$ complexes of naphthalene,[10] anthracene,[11] and the two isomers of phenanthrene.[12] We note in passing that (naphthalene)$Cr(CO)_3$ complexes are very readily reduced to stable dianions[13] and, along with (phenanthrene)$Cr(CO)_3$, are very efficient hydrogenation catalysts.[14] These are topics that are currently being pursued in our laboratories for 1 and other polynuclear (benzenoid)$Cr(CO)_3$ systems.

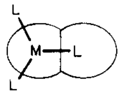


1

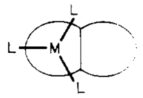


2

Our structural studies of 1 and 2 have been augmented by molecular orbital calculations of the extended Hückel[15] type. Along with a discussion of the bonding in 1 and the related naphthenoid complexes, we have also investigated the conformational preference of the ML_3 group in these and other complexes. Bicyclic (polyene)ML_3 compounds may have two conformational extremes, 3 and 4. We shall call 3 the endo isomer since the symmetry unique L group points to the interior of the uncoordinated portion of the molecule. 4 will then be labeled the exo isomer. With the small steric bulk of the carbonyl ligand and the very small rotational barrier in (benzene)$Cr(CO)_3$[16] one might expect that polynuclear (benzenoid)$Cr(CO)_3$ complexes would show a mixture of endo and exo conformations or, more probably, a range of geometries in the 60° rotation of the $Cr(CO)_3$ group. This is not the case. (Naphthalene)-,[10] (anthracene)-,[11] (phenanthrene)-,[12] and (vide infra) (triphenylene)$Cr(CO)_3$ possess the exo conformation or are structurally very close to it. (Biphenylene)$Cr(CO)_3$ is an outstanding example. It has the endo conformation. We shall develop a theoretical strategy for the analysis of the conformational preference in these $\eta^6Cr(CO)_3$ complexes, as well as for other metal tricarbonyls with different η numbers. We have previously discussed rotational barriers in monocyclic (polyene)ML_3 complexes and conformational effects of reactivity.[17] The propensity of a ML_3 or MCp group to slip from one ring to another in bicyclic polyenes has also been established.[18] Other workers have developed a perturbational approach for which positions the $Fe(CO)_3$, $Cr(CO)_3$, and $Ni(PR_3)_2$ group will coordinate to in polycyclic hydrocarbons.[19]



3



4

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$(\eta^6\text{-}C_{18}H_{12})\text{-}Cr(CO)_3$	$(\eta^6\text{-}C_{12}H_8)\text{-}Cr(CO)_3$
mol wt	364.33	288.23
space group	$C2/m$	$P2_1/m$
cell constants		
a, Å	12.994 (5)	7.065 (4)
b, Å	14.766 (5)	11.066 (5)
c, Å	9.393 (4)	8.030 (4)
β, deg	121.63 (3)	98.43 (3)
cell vol, $Å^3$	1534.5	621.0
molecules/unit cell	4	2
ρ(calcd), g cm^{-3}	1.58	1.54
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.20 × 0.33 × 0.33	0.10 × 0.48 × 0.30
scan width	0.80 + 0.20 tan θ	0.90 + 0.20 tan θ
std reflctns	600, 040	500, 020
decay of standard	±5%	±3%
reflctns measd	1641	1300
2θ range, deg	≤ 50	≤ 50
reflctns collected	944	850
no. of parameters varied	118	91
GOF	1.11	0.62
R	0.023	0.028
R_w	0.027	0.033

Experimental Section

Synthesis of (Biphenylene)tricarbonylchromium. This compound was prepared according to a literature method developed by one of the authors.[20] Large orange, air-stable crystals suitable for X-ray diffraction studies were grown by slow cooling from a heptane solution.

Synthesis of (Triphenylene)tricarbonylchromium and (Triphenylene)hexacarbonyldichromium. Into a nitrogen-flushed, 50-mL 3-necked flask equipped with a stirring bar, gas inlet tube, condenser, and mercury overpressure value was mixed triphenylene (250 mg, 1.1 mmol) with (triamine)tricarbonyl-

---

[9] Chatt, J.; Guy, R. G.; Wetson, H. R. *J. Chem. Soc.* **1961**, 2332.

[10] (a) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* **1967**, *50*, 1052. (b) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1866. (c) Dötz, K. H.; Dietz, R.; von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033. (d) Dietz, R.; Dötz, K. H.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59. (e) Cais, M.; Kaftory, M.; Kohn, D. H.; Tatarsky, D. *J. Organomet. Chem.* **1979**, *184*, 103. Kaftory, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2971. (f) Hall, J. W.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 264.

[11] Hanic, F.; Mills, O. S. *J. Organomet. Chem.* **1968**, *11*, 151.

[12] (a) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, 467. (b) Guss, J. M.; Mason, R. *J. Chem. Soc., Dalton Trans.* **1973**, 1834. (c) Deuschl, H.; Hoppe, W. *Acta Crystallogr.* **1964**, *17*, 800. (d) Lal De, R.; Von Seyerl, J.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1979**, *175*, 185. (e) See ref 10e.

[13] Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R., Jr.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951.

[14] Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27. Also see ref 10e.

[15] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179, 3489; **1962**; *37*, 2872.

[16] (a) Electron diffraction studies indicate that this must be the case: Chiu, N.-S.; Schäfer, L.; Seip, R. *J. Organomet. Chem.* **1975**, *101*, 331. (b) (Benzene)$Cr(CO)_3$ has a conformation where the carbonyls stagger carbon atoms: Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314, 1298. Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2519. However, there are two isoelectronic $\eta^6\text{-}C_6H_6RuL_3$ complexes that have the eclipsed structure and another is staggered: Chan, L. Y. Y.; Graham, W. A. G. *Inorg. Chem.* **1975**, *14*, 1778. Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J. *Ibid.* **1975**, *14*, 3046. Bennett, A.; Robertson, G. B. *J. Organomet. Chem.* **1972**, *43*, C41. This again substantiates a very small barrier.

[17] (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. (c) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1. (d) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *198* 3092. (e) Albright, T. A. *Trans Am. Crystallogr. Assoc.* **1980**, *16*, 35. (f) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

[18] Albright, T. A.; Hofmann, P.; Lillya, C. P.; Dobosch, P. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

[19] (a) Nicholson, B. J. *J. Am. Chem. Soc.* **1966**, *88*, 5156. (b) Herndon, W. C. *Ibid.* **1980**, *102*, 1538. (c) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 20, 26, 31. (d) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884.

[20] Moser, G. A.; Rausch, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 37.

chromium[20,21] (614 mg, 3.3 mmol) in 30 mL of purified dioxane (refluxed over sodium and distilled under nitrogen). The reaction mixture was heated to reflux for 8 h and then filtered under nitrogen on a glass frit. The yellow solid that remained on the frit was extracted with 125 mL of hot tetrahydrofuran, and the extracts were combined with the original yellow filtrate. Alumina (10 g) was added and the solvent removed in vacuo. The dry pack was placed on an alumina column under nitrogen. Initial elution with hexane removed 50 mg (21%) of triphenylene as a colorless band.

Continued elution with ethyl ether removed a light yellow band. Evaporation of the solvent produced 0.19 g (47%) of (triphenylene)tricarbonylchromium as yellow crystals, mp 295–297 °C dec (lit.[22] mp 183–184 °C), suitable for X-ray diffraction studies: MS, *m/e* 364 (M^+). IR (KBr) 1990, 1910 cm^{-1} (ν_{CO}). Anal. Calcd: C, 69.23; H, 3.32. Found: C, 69.23; H, 3.58. The compound was too insoluble for proton NMR measurements. Attempts to recrystallize this product from *n*-butyl ether[22] invariably led to less pure material (mp 180–190 °C).

Finally, elution with tetrahydrofuran eluted a yellow-orange band. Removal of the solvent produced 0.11 g (21%) of (triphenylene)hexacarbonyldichromium in the form of orange crystals, mp 294–296 °C dec. Anal. Calcd: C, 57.60; H, 2.42. Found: C, 57.50; H, 2.56.

(Triphenylene)tricarbonylchromium (2.6 g, mp 296–297 °C dec) could also be prepared in 81% yield from triphenylene (2.0 g, 8.8 mmol), hexacarbonylchromium (1.93 g, 8.8 mmol), *n*-butyl ether (120 mL), and tetrahydrofuran (10 mL), utilizing a 24-h reflux period and similar workup. This method was adapted from an *Inorganic Synthesis* procedure[23] for synthesizing (arene)tricarbonylchromium compounds.

X-ray Data Collection, Structure Determination, and Refinement for (Triphenylene)$Cr(CO)_3$. Single crystals of this compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The possible space groups were determined to be either *C*2, *Cm*, or *C*2/*m*. Successful solution and refinement of the structure showed the correct choice to be centric *C*2/*m*.

Data were collected on a Enraf-Nonius CAD-4 diffractometer by the θ–2θ scantechnique. The method has been previously described.[24] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[25] Neutral atom scattering factors for Cr, O, and C were taken from Cromer and Waber.[26] The scattering for chromium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[27] Scattering factors for H were taken from ref 28.

The position of the chromium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the chromium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.075$. The hydrogen atoms of the triphenylene ligand were placed at calculated positions 1.00 Å from the bonded carbon atom and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.023$ and $R_w = 0.027$. A final difference Fourier showed no feature greater than 0.3 $e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[29]

Table II. Final Positional Parameters

atom	*x/a*	*y/b*	*z/c*
	A. (Biphenylene)$Cr(CO)_3$, **1**		
Cr	0.7059 (1)	0.2500	0.70324 (9)
O(1)	0.6937 (6)	0.2500	1.0737 (4)
O(2)	0.3927 (3)	0.0649 (2)	0.6531 (4)
C(1)	0.6949 (6)	0.2500	0.9307 (6)
C(2)	0.5141 (4)	0.1352 (3)	0.6723 (4)
C(3)	0.8282 (4)	0.1865 (3)	0.4824 (4)
C(4)	0.9178 (4)	0.1187 (3)	0.6226 (4)
C(5)	1.0068 (4)	0.1843 (3)	0.7582 (4)
C(6)	1.1194 (4)	0.1858 (3)	0.9330 (4)
C(7)	1.2012 (5)	0.1198 (3)	1.0682 (4)
C(8)	1.2834 (5)	0.1875 (4)	1.2067 (4)
H(1)[C(3)]	0.7648	0.1424	0.3833
H(2)[C(4)]	0.9173	0.0300	0.6231
H(3)[C(7)]	1.1999	0.0310	1.0673
H(4)[C(8)]	1.3437	0.1442	1.3083
	B. (Triphenylene)$Cr(CO)_3$, **2**		
Cr	0.18599 (6)	0.0000	0.42452 (8)
O(1)	−0.0791 (3)	0.0000	0.1808 (4)
O(2)	0.1557 (2)	0.1438 (2)	0.6235 (3)
C(1)	0.2183 (2)	0.0474 (2)	0.2281 (3)
C(2)	0.2943 (3)	0.0941 (2)	0.3742 (3)
C(3)	0.3771 (2)	0.0479 (2)	0.5256 (3)
C(4)	0.4602 (2)	0.0970 (2)	0.6790 (3)
C(5)	0.4650 (3)	0.1916 (2)	0.6813 (4)
C(6)	0.5451 (3)	0.2371 (2)	0.8240 (5)
C(7)	0.6219 (3)	0.1909 (2)	0.9683 (4)
C(8)	0.6195 (2)	0.0986 (2)	0.9687 (3)
C(9)	0.5392 (2)	0.0495 (2)	0.8257 (3)
C(10)	0.0229 (4)	0.0000	0.2758 (5)
C(11)	0.1664 (2)	0.0879 (2)	0.5473 (3)
H(1)[C(1)]	0.1635	0.0812	0.1228
H(2)[C(2)]	0.2921	0.1611	0.3750
H(3)[C(5)]	0.4085	0.2259	0.5768
H(4)[C(6)]	0.5478	0.3043	0.8237
H(5)[C(7)]	0.6797	0.2246	1.0728
H(6)[C(8)]	0.6759	0.0646	1.0732

Table III. Parameters Used in the Extended Hückel Calculations

orbital type		H_{ii}	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Cr	3d	−11.22	4.95	1.60	0.4876	0.7205
	4s	−8.66	1.70			
	4p	−5.24	1.70			
Mn	3d	−11.59	5.15	1.90	0.5320	0.6490
	4s	−8.63	1.80			
	4p	−5.06	1.80			
Fe	3d	−12.70	5.35	1.80	0.5366	0.6678
	4s	−9.17	1.90			
	4p	−5.37	1.90			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
O	2s	−32.30	2.275			
	2p	−14.80	2.275			
H	1s	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

X-ray Data Collection, Structure Determination, and Refinement for (Biphenylene)$Cr(CO)_3$. The data were obtained and treated in the manner described for the previous compound. The pertinent parameters are given in Table I. From the allowed space groups *P*2, *Pm*, and $P2_1/m$, the latter was found to be the correct choice by the successful solution and refinement of the structure.

---

(21) Rausch, M. D.; Moser, G. A.; Zaiko, E. J.; Lipman, A. L. *J. Organomet. Chem.* **1970**, *23*, 185.

(22) Sato, M.; Ishida, Y.; Nakamura, Y.; Kajiwara, M. *Nippon Kagaku Zasshi* **1970**, *91*, 1188.

(23) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

(24) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(25) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(26) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(27) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(28) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(29) See paragraph at the end of paper regarding supplementary material.

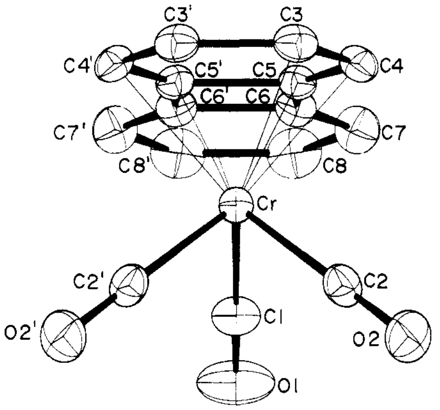


Figure 1. A side view of the structure and numbering system in (biphenylene)$Cr(CO)_3$, 1.

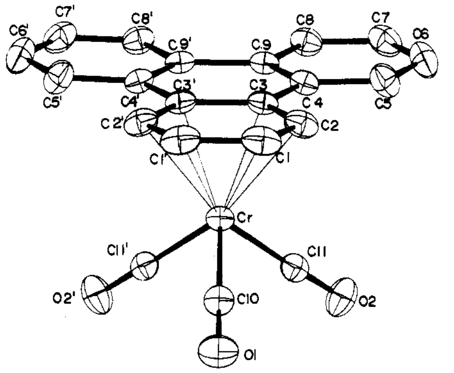


Figure 2. A side view of the structure and numbering system in (triphenylene)$Cr(CO)_3$, 2.

The position of the chromium atom was again found by using a Patterson map. A difference Fourier map phased on the chromium atom afforded the remaining non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = 0.064$. The hydrogen atoms of the biphenylene ligand were placed in calculated positions (1.00 Å) from the bonded carbon atoms, and their parameters were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.028$ and $R_w = 0.033$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[29]

Molecular Orbital Calculations. The extended Hückel calculations used a modified Wolfberg–Helmholtz relationship[30] and a fragment molecular orbital analysis.[31] The H_{ii}'s and orbital exponens are listed in Table III and have been taken from previous work.[17] All C–C, C–O, and C–H distances were idealized at 1.41 (except in the ring junctures of (biphenylene)$Cr(CO)_3$—see text), 1.14, and 1.09 Å, respectively. The M–C(O) distances employed were as follows: Cr, 1.84 Å; Mn, 1.82 Å; Fe 1.78 Å. The metal–ring distances were set at M-η^6-polyene = 1.72 Å, M–η^5 = 1.69 Å, M–η^4 = 1.79 Å. In each case the $M(CO)_3$ group was put in the center of the coordinated ring. All (O)C–M–C(O) angles were idealized at 90°.

Table IV. **Bond Lengths (Å) and Angles (deg) for (Biphenylene)$Cr(CO)_3$, 1**[a]

Bond Lengths

Cr-C(1)	1.839 (5)	Cr-C(2)	1.847 (3)
Cr-C(3)	2.199 (3)	Cr-C(4)	2.249 (3)
Cr-C(5)	2.229 (3)	O(1)-C(1)	1.150 (5)
O(2)-C(2)	1.151 (4)	C(3)-C(4)	1.422 (4)
C(3)-C(3)'	1.406 (7)	C(4)-C(5)	1.381 (4)
C(5)-C(6)	1.508 (4)	C(5)-C(5)'	1.454 (6)
C(6)-C(7)	1.365 (4)	C(6)-C(6)'	1.420 (6)
C(7)-C(8)	1.395 (5)	C(8)-C(8)'	1.383 (8)
cent-Cr	1.721		

Bond Angles

C(1)-Cr-C(2)	89.8 (1)	Cr-C(1)-O(1)	178.0 (4)
Cr-C(2)-O(2)	179.0 (3)	C(2)-Cr-C(2)'	86.9 (2)
C(4)-C(3)-C(3)'	121.8 (2)	C(3)-C(4)-C(5)	116.4 (3)
C(4)-C(5)-C(6)	148.9 (3)	C(4)-C(5)-C(5)'	121.7 (2)
C(6)-C(5)-C(5)'	89.4 (2)	C(5)-C(6)-C(7)	147.0 (3)
C(5)-C(6)-C(6)'	90.6 (2)	C(7)-C(6)-C(6)'	122.3 (2)
C(6)-C(7)-C(8)	115.2 (3)	C(7)-C(8)-C(8)'	122.5 (2)
cent-Cr-C(1)	123.10	cent-Cr-C(2)	127.59

[a] Primed atoms are related by $(x, {}^1/_2 - y, z)$ to those given in Table IIA.

Table V. **Bond Lengths (Å) and Angles (deg) for (Triphenylene)$Cr(CO)_3$, 2**[a]

Bond Lengths

Cr-C(1)	2.209 (3)	Cr-C(2)	2.199 (3)
Cr-C(3)	2.258 (3)	Cr-C(10)	1.827 (4)
Cr-C(11)	1.840 (3)	O(1)-C(10)	1.146 (5)
O(2)-C(11)	1.148 (3)	C(1)-C(2)	1.383 (4)
C(1)-C(1)'	1.399 (7)	C(2)-C(3)	1.429 (4)
C(3)-C(4)	1.461 (4)	C(3)-C(3)'	1.416 (6)
C(4)-C(5)	1.397 (4)	C(4)-C(9)	1.401 (4)
C(5)-C(6)	1.367 (4)	C(6)-C(7)	1.371 (5)
C(7)-C(8)	1.363 (4)	C(8)-C(9)	1.395 (4)
C(9)-C(9)'	1.462 (5)	cent-Cr	1.720

Bond Angles

C(10)-Cr-C(11)	89.6 (1)	C(2)-C(1)-C(1)'	119.9 (2)
C(1)-C(2)-C(3)	121.5 (3)	C(2)-C(3)-C(4)	121.7 (3)
C(2)-C(3)-C(3)'	118.5 (2)	C(4)-C(3)-C(3)'	119.7 (1)
C(3)-C(4)-C(5)	121.0 (3)	C(3)-C(4)-C(9)	120.2 (2)
C(5)-C(4)-C(9)	118.8 (3)	C(4)-C(5)-C(6)	120.8 (3)
C(5)-C(6)-C(7)	120.6 (3)	C(6)-C(7)-C(8)	119.6 (3)
C(7)-C(8)-C(9)	121.6 (3)	C(4)-C(9)-C(8)	118.6 (3)
C(4)-C(9)-C(9)'	120.1 (2)	C(8)-C(9)-C(9)'	121.3 (2)
Cr-C(10)-O(1)	179.1 (4)	Cr-C(11)-O(2)	178.7 (3)
C(11)-Cr-C(11)'	89.7 (2)	cent-Cr-C(10)	126.33
cent-Cr-C(11)	125.11		

[a] Primed atoms are related by $(x, -y, z)$ to those given in Table IIB.

Description of the Structures

The structure and numbering system employed for (biphenylene)$Cr(CO)_3$, 1, and (triphenylene)$Cr(CO)_3$, 2, is displayed in Figures 1 and 2, respectively. A listing of the relevant bond distances and angles for 1 and 2 are given in TableIV and V, respectively. The geometry of the $Cr(CO)_3$ groups for both compounds is unremarkable in comparison to other (arene)$Cr(CO)_3$ complexes.[32] The pattern of Cr–arene distances found for (triphenylene)-$Cr(CO)_3$, 2, is also typical of that observed for other polynuclear (benzenoid)$Cr(CO)_3$ complexes.[32] Namely, the Cr–C1 distance of 2.209 (3) Å is significantly shorter than that to the carbon at the ring junction (Cr–C3 = 2.258 (3) Å). This also occurs in (biphenylene$Cr(CO)_3$, 1, i.e., Cr–C3 = 2.199 (3) Å vs. Cr–C_5 = 2.229 Å. The longer Cr–C4 distance in 1 (2.249 (3) Å) is due to the fact that the C3–C4 bond is somewhat lengthened in comparison to C3–C3′ and C4–C5, and the C3–C4–C5 angle is rather acute (116.4 (2)°). This distortion also occurs in the free biphenylene ligand.[8] Thus, in 1 and 2 the $Cr(CO)_3$ group is shifted somewhat from an idealized η^6 position away from the ring

---

[30] Ammeter, J. H.; Bügi, H. B., Thibeault, J. C.; Hoffmann, R. *J. Chem. Phys.* **1976**, *100*, 3686.

[31] Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Chem. Phys.* **1973**, *95*, 7644. Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167.

[32] For a review see: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

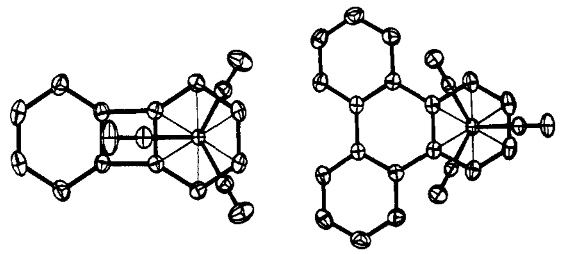


Figure 3. A top view of (biphenylene)- and (triphenylene)Cr(CO)$_3$.

junction. This basically is related to the ability for a Cr(CO)$_3$ group to shift from one ring to another. The details will not be given here.[18] In both of these cases the activation energies for ring shifting are tremendously high; they are forbidden haptotropic shifts.[18] With this steep potential rise, the ground-state minima are shifted toward an η^4-coordination mode in the opposite direction.

The biphenylene and triphenylene ligands in 1 and 2, respectively, are not much distorted from planarity. For example, the greatest deviation from the best plane in 1 occurs for C7 and C8 which lie 0.04 and 0.08 Å, respectively, from the plane. Biphenylene itself shows a significant C–C single and double localization.[8] This is diminished in the complex. Most notably the C3–C3′ and C4–C5 bonds are lengthened while the C7–C8 bond length is shortened in comparison to the crystallographic results for biphenylene.[8a] The bond localization is not, however, totally removed in 1. There is, for example, a significant long–short–long pattern in the C3–C4, C4–C5, and C5–C5′ bond lengths. We will return to the electronic rationale for these results in the next section, but we note that this trend is in agreement with the ^{13}C and ^{1}H NMR data for 1 reported by Venzo and co-workers.[33] Their NMR results suggest that there is a substantial reduction in the bond fixation (paratropic character) on going from free biphenylene to complex 1.

A particularly interesting feature about the structure of 1 and 2 is the orientation the Cr(CO)$_3$ unit with respect to the benzenoid ring. A top view of both complexes is presented in Figure 3. It can be clearly seen that (triphenylene)Cr(CO)$_3$ adopts the exo conformation (4) while (biphenylene)Cr(CO)$_3$ is of the endo type (3). As mentioned in the Introduction, the orientation of (triphenylene)Cr(CO)$_3$ is identical with that found for all other polynuclear (benzenoid)Cr(CO)$_3$ complexes.[10-12,32] The endo conformation for (biphenylene)Cr(CO)$_3$ is unprecedented. We contend that these orientational preferences have an electronic origin which is discussed in the following section.

Electronic Structure of (Biphenylene)- and (Naphthalene)Cr(CO)$_3$

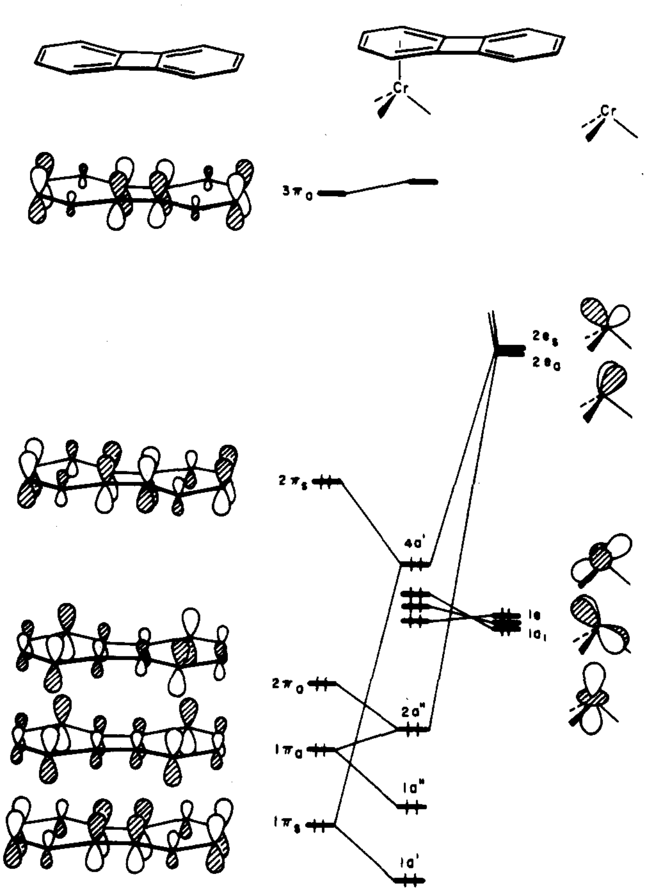


Figure 4. An orbital interaction diagram for (biphenylene)Cr(CO)$_3$.

5

6

Extended Hückel calculations were carried out on (biphenylene)Cr(CO)$_3$ and (naphthalene)Cr(CO)$_3$ as a model for 2. Computational and geometric details are given in the Experimental Section. Our approach in developing the orbitals of these complexes is to allow the important valence orbitals of Cr(CO)$_3$ to interact with the arene. Figure 4 shows orbital interaction diagram for (biphenylene)Cr(CO)$_3$. The orbitals of Cr(CO)$_3$ have been extensively discussed elsewhere,[17,34] and we will only point out the salient features. Lying at higher energy are two degenerate orbitals, labeled 2e. Their shape can be derived by considering the removal of three carbonyls from octahedral Cr(CO)$_6$, 5. The resulting Cr(CO)$_3$ fragment will have three empty orbitals that point toward the missing carbonyls. Symmetry adapted linear combinations of the three in 6 give a higher lying[35] a_1 level, not shown in Figure 4, and the 2e set. An alternative way to view 2e is that it is the remnant of the octahedral e_g set in 5. Therefore, it is mainly d_{z^2} and $d_{x^2-y^2}$, using the normal coordinate system in 5. The symmetry in Cr(CO)$_3$ is lower than that in Cr(CO)$_6$. This means that metal p mixes into what was e_g to hybridize the orbitals out away from the remaining carbonyls. Each member of the 2e set will be used extensively; therefore, we have labeled them $2e_s$ and $2e_a$ depending on whether the orbital is symmetric or antisymmetric, respectively, to the mirror plane of the paper. 1e and $1a_1$ are derived from t_{2g} in Cr(CO)$_6$. The removal of three carbonyls does not significantly change their shape. Therefore, 1e and $1a_1$ are bonding with respect to the carbonyl π^* orbitals. An important point to be made is that 2e and 1e are "tilted".[17a] That is, in Figure 4, the radial extent of $2e_s$ and $2e_a$ are *not* left–right symmetric. $2e_a$ is concentrated more toward the right side, over the symmetry unique carbonyl. The titlting of $2e_s$ is in the opposite direction—on the left side. This tilting can be seen to be a natural outgrowth of the fact that the Cr(CO)$_3$

---

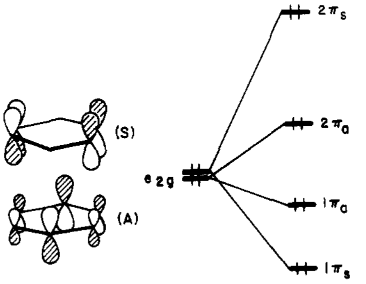
[33] Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1982**, *239*, 345.

[34] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148. Burdett, J. K. *Ibid.* **1975**, *14*, 375.

[35] The a_1 combination lies higher than e because it is primarily comprized of metal s and p, whereas e is mainly metal d; see ref 34.

orbitals remember their octahedral parentage. We have exploited this tilting previously[17] for setting conformatinal preferences in (polyene)ML_3 complexes. It will figure heavily into the discussion here, as well.

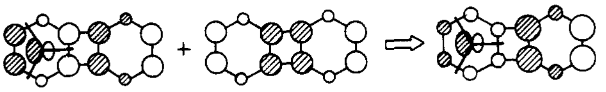
Only the important π orbitals of biphenylene are shown on the left of Figure 4. Here again we have labeled them with a subscript which refers to their symmetry with respect to the mirror plane. $1\pi_s$ through $2\pi_s$ are recognizable as the bonding and antibonding combinations of the e_{2g} set of benzene π orbitals. They are split as shown in 7.



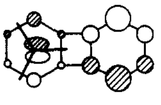
7

The S component of e_{2g} is split to a far greater extent than the A component. This is due to the larger atomic coefficients at the two carbons which are fused to the other benzene ring for S compared to A.[36] There is also a small amount of mixing from the other π orbitals of benzene. This causes minor polarizations of the magnitudes of the atomic coefficients which are especially evident in $1\pi_s$ and $2\pi_s$ at the carbons containing the nodal plane in e_{2g}(S). $2\pi_s$ is, therefore, the highest lying π orbital and will interact with the empty 2e set to the greatest extent.

Returning to Figure 4, 1e and $1a_1$ are largely nonbonding. One component of 1e is slightly stabilizing by the LUMO, $3\pi_a$, however, both components are destabilized by high-lying ring σ orbitals, also of δ symmetry. The empty 2e set of $Cr(CO)_3$ stabilizes $1\pi_s$, $1\pi_a$, $2\pi_a$, and $2\pi_s$. These combinations contain by far the most significant interactions in the complexation of $Cr(CO)_3$ to biphenylene. Notice that $2\pi_s$ and $1\pi_s$ combine with $2e_s$. There are three interacting fragment orbitals. The middle level, 4a′, by the typical considerations of perturbation theory,[37] is the bonding interaction between $2\pi_s$ and $2e_s$, with some $1\pi_s$ mixed in an antibonding manner. A convenient top view is illustrated by 8. Most of the electron density is contained within the uncoordinated benzene ring. The same analysis for the $1\pi_a$, $2\pi_a$ interaction with $2e_a$ gives 9 as the middle orbital—2a″ in Figure 4. In the molecular levels 1a′ and 1a″ most of the electron density is localized on the coordinated portion of biphenylene. What we are describing in molecular orbital terms is that the $Cr(CO)_3$ group complexes one benzenoid set of π orbitals, leaving behind a set of π orbitals that resemble those in free benzene. In other words the localization in biphenylene is broken. This is observable, expecially in the shortening of C7–C8 and lengthening of C4–C5 and C3–C3′ bonds (see Figure 1 for the labeling scheme). However, the localization is not totally broken, in other words, especially the intermixing between $1\pi_s$ and $2\pi_s$ is not complete. We shall shortly return to this point.

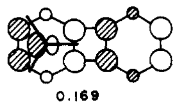


8

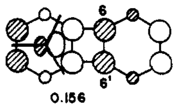


9

The preceding discussion was done without regard to the conformation of the $Cr(CO)_3$ group. As we have pointed out previously the dominant interaction between the filled π orbitals of biphenylene and 2e on $Cr(CO)_3$ is with $2\pi_s$. A top view of the interaction in the endo (10) and exo (11) conformations are shown below. Also listed is the overlap integral between $2e_s$ and $2\pi_s$ for each rotomer. The overlap in the exo conformation is smaller. $2e_s$ has its greatest extent on the side opposite to the symmetry unique carbonyl. Therefore, the antibonding to C6 and C6′ is larger in 11 than in 10. This effect should be sensitive to the C5–C6 and C5–C6 distances. Our calculations reflect this. When the distance is 1.51 Å, corresponding to the observed structure, the barrier was calculated to be 0.8 kcal/mol favoring the endo conformation. Reducing the distance to 1.41 Å raises the barrier to 1.2 kcal/mol. These are quite small barriers; the reason behind this is that the tilting in $2e_a$ causes a smaller overlap with $2\pi_a$ in the endo vs. exo conformation.[38] Thus, part of the conformational preference is removed. We shall see other systems where the tilting in both members of 2e operate in concert and the barriers are larger.



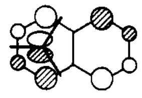
vs



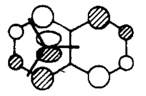
$\langle 2e_s|2\pi_s\rangle =$ 0.169 0.156

10 11

Figure 5 shows the orbital interaction diagram for (naphthalene)$Cr(CO)_3$. Here again the 1e + $1a_1$ set is largely nonbonding. The $Cr(CO)_3$ 2e set stabilizes $1\pi_a$, $2\pi_a$, and $1\pi_s$, giving 1a″, a′, and 2a″. Again 2a″ is concentrated mostly on the uncoordinated portion of the naphthalene. 2a″ then resembles the second π orbital of butadiene. It can be seen that the $Cr(CO)_3$ partially uncouples an η^6 ring leaving behind a butadiene. Bond lengths in the available structures[10] indicate this tendency. Here the overlap of $2e_a$ with $2\pi_a$, the dominant interaction, is favored in the exo conformation 12 vs. 13. It is the increased antibonding between the tilted $2e_a$ orbital and the adjacent noncoordinated carbons that sets the differential. The $1\pi_s$, $2e_s$ combination is not significantly altered in the rotation. Our calculations give a barrier of 2.5 kcal/mol favoring the exo geometry.



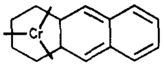
vs



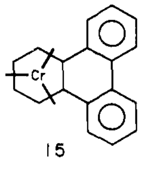
$\langle 2\pi_a|2e_a\rangle =$ 0.178 0.158

12 13

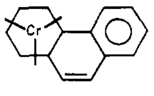
The preferred exo conformations of anthracene,[11] 14, triphenylene, 15, and the η^6-1,4,11,12-isomer of (phenanthrene)$Cr(CO)_3$,[12] 16, are straightforward analogies. Fusion of additional butadiene linkages to the naphthalene



14



15



16

---

[36] The cross overlap between diagonal carbons at the junction of the two rings also favor S over A.

[37] Hoffmann, R. *Acc. Chem. Res.* 1971, *4*, 1.

[38] The conformational effects on the $2e_s$–$1\pi_s$ and $2e_a$–$1\pi_a$ overlaps are also mutually opposite and essentially cancel each other.

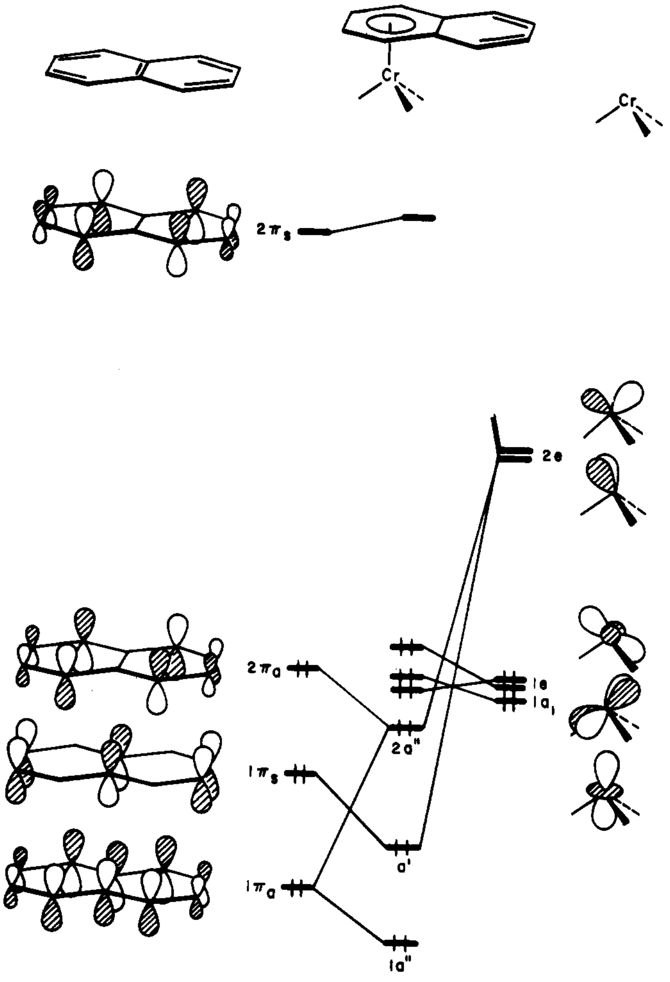
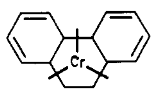
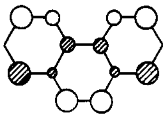


Figure 5. An orbital interaction diagram for (naphthalene)Cr(CO)$_3$.

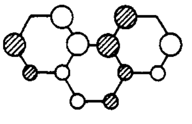
skeleton does not affect the analysis. Complexation of the Cr(CO)$_3$ group tends to give the localization (or delocalization) indicated in **14–16**. The conformation observed[12b] for the (9–14-η^6-phenanthrene)Cr(CO)$_3$ isomer, **17**, can



17

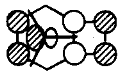


18

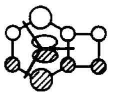


19

likewise be viewed from maximization of the overlap of 2e with the two highest occupied π levels, **18** and **19**. The tilting in both members of 2e favor **17**. (Benzocyclobutadiene)Cr(CO)$_3$ we predict will favor the endo geometry by 3.5 kcal/mol. **20** and **21** show that the differential is



20

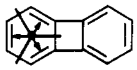


21

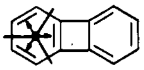
set by the decreased antibonding between 2e$_s$ and the noncoordinated olefinic portion in benzocyclobutene at the endo geometry (**20**) and the increased bonding between 2e$_a$ and the olefinic group (**21**). Thus, in contrast to (biphenylene)Cr(CO)$_3$ both interactons favor the endo conformation and a larger rotational barrier is computed for it. The preparation and structural determination of a (benzocyclobutene)Cr(CO)$_3$ complex is eagerly awaited to test this prediction.

Other Bicyclic (Polyene)ML$_3$ Complexes

One could construct another argument concerning the endo preference of (biphenylene)Cr(CO)$_3$ by recalling that the spatial extension of the three empty orbitals in Cr(CO)$_3$ (see **6**) is set up to reconstruct an octahedral geometry. With the endo geometry, the Cr(CO)$_3$ can tie up three carbon–carbon double bonds, as shown in **22**. The arrows



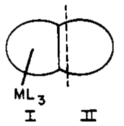
22



23

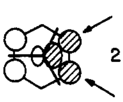
show the orientation of the three acceptor orbitals on chromium. Notice that this uses the favored resonance structure of biphenylene in contrast to the one in **23** for the exo geometry. The emphasis here is put on the ability of the Cr(CO)$_3$ group to localize carbon–carbon double and single bonds in (arene)Cr(CO)$_3$ compounds. This has been structurally observed for (benzene)Cr(CO)$_3$.[16b,39] It appears in molecular orbital calculations[17a] and has been explained on the basis of perturbation theory.[40] The same operation can be employed, albeit with more difficulty, for the naphthalene, etc. cases. In discussing η^5 or η^4 bicyclic (polyene)ML$_3$ complexes this localized scheme does not apply well. One could, if all else fails, proceed through a differential overlap argument starting from the π levels of the polyene as was done in the previous two sections; however, there is a simpler perturbation based approach to the problem.

Consider each bicyclic complex to be constructed from two sections, as indicated by the dashed line in **24**. One

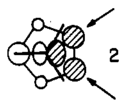


24

section consists of the (polyene)ML$_3$ group labeled I; the other is a noncoordinated acyclic polyene, II. I has two bonding levels corresponding to the in-phase interaction between 2e and the π (or π^*) levels of the polyene.[17a] These are shown for an η^6-benzene system in **25**, η^5-cyclopentadienyl in **26**, and η^4-cyclobutadiene in **27**. The arrows serve to remind us at which point II fuses to I. It should be noted that there is free rotation in each of the parent systems.[17a] **25–27** will be interacted with either the highest lying occupied orbitals or (and) the lowest lying unoccupied orbitals of **II**. There are two cases: if the orbital on II is empty then it will interact with **25–27** in a bonding manner and the Cr(CO)$_3$ unit will rotate its axis to maximize that component of 2e with the LUMO of II. If the orbital on II is filled, then **25–27** will interact with I in an antibonding manner.[41] In this case Cr(CO)$_3$ will

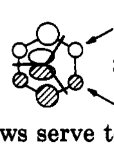


25a

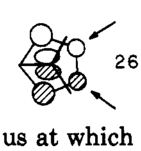


26a

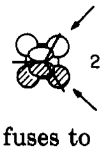
27a



25b



26b



27b

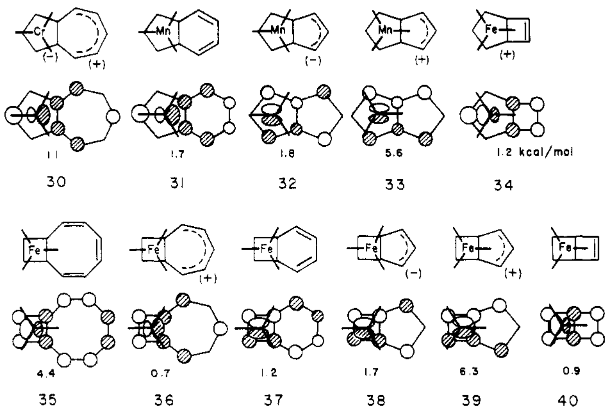
---

(39) See also η^6-Me$_6$C$_6$-Mo(CO)$_3$: Koshland, D. E.; Myers, S. E.; Chesick, J. P. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2013.

(40) Chinn, J. W., Jr.; Hall, M. B. *J. Am. Chem. Soc.*, in press.

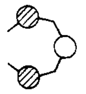
(41) This will be the stereochemically dominant interaction whether or not **25–27** lie energeticaly below the HOMO of II.

Chart I

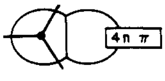


orient itself to minimize its interaction with II. Normally favored interactions with **25a–27a** and **25b–27b** orient the $Cr(CO)_3$ in the same direction ((biphenylene)$Cr(CO)_3$ is the only exception that we have encountered). However, the problem can be simplified still further; usually only one of the two members of **25–27** needs to be interacted. This will always be that member which the orbital of II perturbs the most. This is easy to determine when II contains an odd number of carbons. The nonbonding orbital, **28** for the allyl system and **29** for the pentadienyl

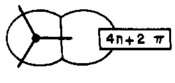

28


29

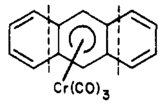
one, will perturb **25–27** to the greatest extent. The π orbital of an olefin and HOMO of a hexatriene linkage will also do the same. A butadiene linkage is difficult to determine, both the HOMO and LUMO will significantly perturb **25–27**. A point can also be made about the importance of the pairs of interactions in I. The very small coefficients at the ring junction in **25b** tend to make any perturbation of **25a** larger. **27a** and **27b** are obviously both equally affected baring any other factor. The situation for **26a** and **26b** is intermediate, with **26a** being slightly more favorable. With these points in mind, the conformations of the molecules in Chart I were constructed. Below it is shown the dominant perturbation of I by II. Also listed are the calculated rotational barriers in kilocalories per mole. In each instance our calculations match the conformation picked by this perturbational method. Furthermore, the observed geometries for **30**,[42] **31**,[43] and **37**[6,44] are in agreement with those shown in Chart I. Compounds **35**,[45] **36**,[46] and **38**,[47] have been prepared but their structure has not been determined. (Biphenylene)-, (naphthalene)-, and (benzocyclobutadiene)$Cr(CO)_3$ also fit this pattern. Notice that in **33** the interaction of **28** to **26b** is bonding since we use the allyl cation. In **32** this is reversed; now **28** is filled and interacts with **26b** in an antibonding manner. The same dichotomy is present in **38** and **39**. One caveat should be inserted here. I in **24** must always be an 18-electron, saturated complex for the purpose of assigning an electron count to II. This ensures that both members of **25–27** will be filled. One final simplification can be constructed given the nodal structure of π orbitals. The conformation of (naphthalene)$Cr(CO)_3$, **31**, and **37** are identical; the exo geometry is preferred. Likewise, (benzocyclobutadiene)$Cr(CO)_3$, **34**, and **40** favor the endo conformation. In general, when II contains $4n$ π electrons, the exo geometry is favored, and when II contains $4n + 2\pi$ electrons the endo conformation is preferred. This is summarized schematically in **41** and **42**. More complicated cases like the (phenanthrene)$Cr(CO)_3$ isomer, **17**, can be handled by noting the preferred conformation when each butadiene unit perturbs I in turn. Thus, an isomer of (anthacene)$Cr(CO)_3$, **43**, will have no conformational preference. The butadienoid units in **43** use **41** in an opposing fashion.



41



42



43

Acknowledgment. T.A.A. wishes to thank the Robert A. Welch Foundation, Research Corp., and the Scientific Affairs Division of NATO for generous support and the hospitality of Dr. Peter Hofmann at Erlangen where this manuscript and some of the work was completed. J.L.A. and M.D.R. thank the National Science Foundation for support of this work.

Registry No. 1, 53415-77-3; 2, 32801-42-6; (triphenylene)hexacarbonyldichromium, 87801-24-9; (triamine)tricarbonylchromium, 14974-11-9; hexacarbonylchromium, 13007-92-6; (naphthalene)tricarbonylchromium, 12110-37-1.

Supplementary Material Available: Listings of the thermal parameters and structures factor amplitudes for compounds 1 and 2 (13 pages). Ordering information is given on any current masthead page.

---

[42] Koch, O.; Edelmann, F.; Behrens, U. *J. Organomet. Chem.* **1979**, *168*, 167.

[43] Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. A. *J. Organomet. Chem.* **1979**, *179*, 403; Shakir, R.; Atwood, J. L. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1656.

[44] (a) Riley, P. E.; Davis, R. E. *Organometallics* **1983**, *2*, 286. (b) Butters, T.; Toda, F.; Winter, W. Angew. *Chem.* **1980**, *92*, 952. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 926, Winter, W.; Butters, T. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1528. Butters, T.; Winters, W.; Toda, F. *Ibid.* **1981**, *B37*, 1532.

[45] Magon, M.; Schröder, G. *Liebigs Ann. Chem.* **1978**, 1379.

[46] (a) Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1977**, 65. (b) Hall, S. R.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 1691.

[47] Bamberg, J. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 3173.