Volume 19
Number 2
February 1980

Inorganic Chemistry

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Structural Analysis of (Pentamethylcyclopentadienyl)cobalt(I) Dicarbonyl: Evidence for an Electronically Induced Distortion of the Cyclopentadienyl Ring due to Its Interaction with a Planar $Co(CO)_2$ Fragment[1]

LANCE R. BYERS and LAWRENCE F. DAHL*

Received May 2, 1979

A relatively precise crystallographic analysis of $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$, in which the cyclopentadienyl ring has been effectively anchored from librational motion by the methyl substituents, has provided convincing evidence (in accord with our hopeful expectations) for a statistically significant and theoretically meaningful distortion of the cyclopentadienyl ring due to its noncylindrical bonding interaction with a sterically innocent, planar ML_2 fragment. The entire molecule conforms within experimental error to bilateral symmetry with the molecular mirror plane bisecting the $Co(CO)_2$ fragment which is perpendicularly disposed to the cyclopentadienyl ring. The determined distorted C(ring)–C(ring) bond-length pattern consists of two adjacent intermediate bonds of 1.407 (6) and 1.414 (6) Å separated from one shorter bond of 1.392 (6) Å by two longer bonds of 1.447 (6) and 1.445 (6) Å. This small but marked deformation of a cyclopentadienyl ring from a regular pentagonal geometry toward an "allyl–ene" geometry (with a concomitantly slight bending deformation about the two "terminal allyl" ring atoms away from the cobalt atom) may be readily attributed to a resulting localized distribution of p_π electron density on the cyclopentadienyl ring arising primarily from a breakdown of the doubly degenerate e_1 ring orbital degeneracy due mainly to an extensive electron delocalization from the e_1^+ ring component into the empty in-plane d AO of the planar d^8 cobalt(I) dicarbonyl system. This structural study thereby furnishes the first experimentally definite evidence for a clear-cut ring distortion by a planar ML_2 fragment; the crystal structure of dicyclopentadienyl[2,2′-bis(π-allyl)]dinickel, containing two centrosymmetrically related nonplanar $Ni(\eta^3\text{-allyl})$ fragments, each coordinated to an unsubstituted cyclopentadienyl ring, is the only other statistically significant example (to our knowledge) possessing a similar cyclopentadienyl ring deformation. The molecular compound $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ crystallizes in a centrosymmetric monoclinic unit cell of symmetry $P2_1/n$ with $a = 7.507$ (2) Å, $b = 10.770$ (2) Å, $c = 15.288$ (4) Å, $\beta = 97.92$ (2)°, $V = 1224.1$ (5) Å^3, and ρ(calcd) = 1.357 g·cm^{-3} for $Z = 4$. Full-matrix least-squares refinement with varying positional and anisotropic thermal parameters for the nonhydrogen atoms and varying positional and isotropic temperature parameters for the hydrogen atoms converged at $R_1(F) = 6.40\%$ and $R_2(F) = 6.91\%$ for the 2509 independent diffractometry data ($I \geq 2\sigma(I)$) collected with Mo Kα radiation over the range $3.0° \leq 2\theta \leq 70.0°$. The standard deviation in an observation of unit weight was 1.48, while the ratio of the number of refined observations to the number of variable parameters was 2509/196 = 12.8.

Introduction

The research reported here was an outgrowth of previous structural evidence[2] for localized distortions within a cyclopentadienyl ring due to its coordination with a metal atom which has a noncylindrically symmetric distribution of bonding orbitals. Unfortunately, the electronic implications of the determined variations in the C(ring)–C(ring) bond lengths of certain cyclopentadienyl metal complexes have been clouded by associated large librational motions of the cyclopentadienyl rings (as indicated from the sizes, shapes, and orientations of the thermal ellipsoids of the carbon atoms). Even though a number of structures[2] have pointed toward a breakdown in the idealized C_{5v}-$5m$ geometry of the cyclopentadienyl ligand, the determined librational motion of the ring in the solid state consistently increases the positional uncertainties of the individual carbon atoms such that any statistical significance of the bond-length differences is lost.[3] In fact, the lack of precise crystallographic data led Wheatley[4] to proclaim in 1967 that "the present position concerning distortions in the C(ring)–C(ring) distances in π-bonded aromatic systems is most unsatisfactory" and to raise the question "whether such distortions have indeed been detected".

The librational motion in a cyclopentadienyl ring may be decreased either by carrying out the structural analysis at low temperature and/or by anchoring the cyclopentadienyl ring with nonhydrogen substituents. The latter tactic requires a pentareplacement of the hydrogen atoms with sterically innocent substituents in order not to alter the fivefold symmetry of the ring before its interaction with an appropriate ML_n fragment which may be presumed to produce a given kind of ring distortion.

---

(1) Based in part upon a dissertation submitted by L. R. Byers to the Graduate School of the University of Wisconsin—Madison in partial fulfillment of the requirements of the Ph.D. Degree, May 1978.

(2) (a) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963); (b) M. R. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965); (c) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature (London)*, **201**, 1318 (1964); (d) M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965); (e) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).

(3) (a) M. F. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973), and references cited therein; (b) I. Bernal, J. D. Korp, and G. M. Reisner, *J. Organomet. Chem.*, **139**, 321 (1977), and references cited therein.

(4) P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967), and references therein.

0020-1669/80/1319-0277$01.00/0 © 1980 American Chemical Society

In the course of our research[5] with mixed-metal triangular organometallic complexes, (pentamethylcyclopentadienyl)cobalt dicarbonyl, first prepared and characterized by King and Bisnette,[6] was isolated. The fact that its infrared spectrum in solution is essentially identical with that of the parent compound, $Co(\eta^5\text{-}C_5H_5)(CO)_2$, points to similar molecular configurations. Since this relatively stable compound is also a solid at room temperature in contrast to the ring-unsubstituted parent which is a light-sensitive liquid, a single-crystal X-ray diffraction study was undertaken both to ascertain the presumed overall architecture[7] of this basic organometallic structural unit and to elucidate any geometrical effects resulting from the noncylindrically symmetric interaction of the $Co(CO)_2$ fragment with a librationally damped cyclopentadienyl ring.

The particular interaction of a pentamethylcyclopentadienyl ring with a planar $Co(CO)_2$ fragment appeared to offer an ideal operational test of whether any observed ring distortion could be attributed solely to electronic effects. First, *intramolecular* steric interactions were viewed as being minimal due to the expected disposition of the two terminal carbonyl ligands away from the $C_5(CH_3)_5$ ring. The implicit assumption that electronic effects would dominate over *intermolecular* van der Waals forces in generating bond-length variations of the ring carbon atoms from regular pentagonal symmetry also seemed reasonable. Second, the kind and degree of an electronically induced ring distortion could be readily anticipated from the determined orientation of the ring relative to the $Co(CO)_2$ plane due to the unambiguous directional interaction of the electron-donating ring orbitals with the empty in-plane metal orbitals of the d^8 Co(I). Furthermore, the π-acidic carbonyl ligands were presumed to minimize any back-bonding from the cobalt atom to the $C_5(CH_3)_5$ ring. Third, on the basis of the assumption that the electron-releasing methyl substituents would lead to a stronger orbital interaction of a $C_5(CH_3)_5$ ring with the $Co(CO)_2$ fragment than that of a C_5H_5 ring, it was felt that the degree of an electronically produced ring distortion would possibly be magnified in crystalline $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$.

Herein are presented the structural results which fulfill all expectations in providing convincing evidence that the observed C–C bond-length trend in this case is in complete accord with that predicted from simple qualitative theoretical considerations. It is noteworthy that this concept of noncylindrical metal–cyclopentadienyl bonding giving rise to localization of π-electron density in the ring with concomitant ring deformation was first put forth by Dahl and Wei[2a] in 1963 for the same type of complex (viz., one containing a d^8 Ni(II) coordinated to only two other ligands besides the cyclopentadienyl ring).

Experimental Section

Preparation and Properties. Pentamethylcyclopentadiene was synthesized by the method of Threlkel and Bercaw.[8] $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ was produced via a preparative route described by Rausch and Genetti[9] for a variety of mono(ring-substituted cyclopentadienyl)cobalt dicarbonyl compounds. With the use of standard Schlenk techniques together with a nitrogen atmosphere, 1.71 g (5 mmol) of dicobalt octacarbonyl (Strem Chemical Co.) and 1.64 mL (1.36 g, 10 mmol) of pentamethylcyclopentadiene in 30 mL of methylene chloride were refluxed for 21 h. The solvent was removed in vacuo and the residue extracted with hexane onto an alumina (5 wt % H_2O added) column packed by use of hexane. Elution of the first dark orange band with hexane yielded the desired material. An infrared spectrum (Perkin-Elmer 267 grating infrared spectrophotometer) in hexane solution exhibited two intense carbonyl stretching frequencies at ca. 2010 and 1950 cm^{-1}, corresponding to those reported in cyclohexane at 2011 and 1949 cm^{-1} by King and Bisnette.[6]

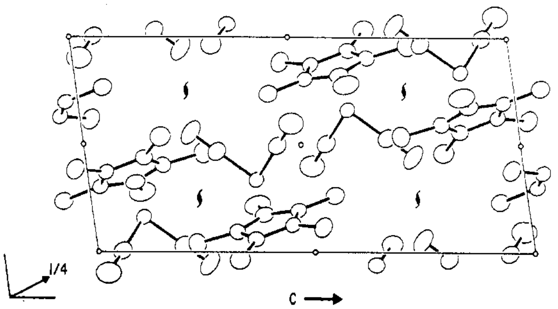


Figure 1. [010] projection of $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ showing the four symmetry-related molecules in a monoclinic unit cell of $P2_1/n$ symmetry. Hydrogen atoms have been omitted for clarity.

Confirmation of the compound's molecular formulation was afforded by a mass spectrum.[10] The molecular ion's observed isotopic abundance pattern compares favorably with that calculated theoretically[11] (in parentheses) at *m/e* 250, 251, and 252 with relative intensities 100.00 (100.00), 12.85 (13.74), and 1.16 (1.28), respectively. The presence of strong peaks in the spectrum corresponding to $Co[C_5(CH_3)_5](CO)^+$ (*m/e* 222) and $Co[C_5(CH_3)_5]^+$ (*m/e* 194) mimics the previously observed mass spectrum of $Co(C_5H_5)(CO)_2$ in which dissociation of the carbonyls in preference to the cyclopentadienyl ring was found to occur.[12] Unlike $Co(C_5H_5)(CO)_2$ for which an ionic fragment analogous to the cyclopropenylcobalt ion, $Co(C_3H_3)^+$, was detected,[12] the corresponding $Co[C_3(CH_3)_3]^+$ fragment (*m/e* 140) was absent. One particularly interesting feature was the appearance of a peak at *m/e* 444 with a relative intensity of 1.75 (vs. the base peak of 100.00); this peak can be assigned to the $\{Co[C_5(CH_3)_5](CO)\}_2^n$ cation ($n = +1$). The analogous neutral dimer ($n = 0$)[13,14] and corresponding monoanion ($n = -1$)[14] have been recently isolated and structurally analyzed.

Single-Crystal X-ray Data Collection. Single crystals of the compound were grown by slow sublimation in vacuo at ca. 40 °C in a 30 cm (length) × 22 mm (diameter) straight glass tube which was surrounded by a 15 cm (long) × 30 mm (diameter) piece of copper tubing, used to create a more uniform and extended temperature gradient and to partially exclude ambient lighting due to the known photolytic instability of the analogous parent compound, $Co(C_5H_5)(CO)_2$.

A moderately large, dark red parallelepiped of approximate dimensions 0.60 mm × 0.60 mm × 0.30 mm was chosen, fixed to a glass fiber with epoxy cement, oriented in an argon-filled Lindemann glass capillary, and mounted on a goniometer. The X-ray measurements were made on a NOVA-automated Syntex $P\bar{1}$ diffractometer with Mo $K\bar{\alpha}$ radiation ($\lambda(\alpha_1) = 0.709\,26$ Å, $\lambda(\alpha_2) = 0.713\,54$ Å).[15] After optical alignment of the crystal, a Polaroid rotation photograph was taken via a slow ϕ scan with $2\theta = \omega = \chi = 0.00°$. Fifteen independent reflections chosen from the photograph were computer centered. The resulting angular coordinates were autoindexed, from which a monoclinic cell was found and confirmed by axial photographs. Least-squares refinement of the angular coordinates of these 15

---

(5) L. R. Byers, V. A. Uchtman, and L. F. Dahl, to be submitted for publication.

(6) R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, **8**, 287 (1967).

(7) (a) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); F. A. Cotton, A. D. Liehr, and G. Wilkinson, *ibid.*, **1**, 175 (1955). (b) The proposed "gross" configuration[7a] of $Co(\eta^5\text{-}C_5H_5)(CO)_2$ has just been substantiated in the gaseous state by an electron diffraction study (B. Beagley, C. T. Parrott, V. Albrecht, and G. G. Young, *J. Mol. Struct.*, **52**, 47 (1979)).

(8) R. S. Threlkel and J. E. Bercaw, *J. Organomet. Chem.*, **136**, 1 (1977).

(9) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).

(10) The mass spectrum was graciously run by Mr. R. B. Randall (University of Wisconsin—Madison) on an AEI MS 902C high-resolution mass spectrometer.

(11) L. R. Byers, "MSEG, a FORTRAN Mass Spectral Envelope Generator", Ph.D. Thesis, University of Wisconsin—Madison, 1978, Appendix I.

(12) R. E. Winters and R. W. Kiser, *J. Organomet. Chem.*, **4**, 190 (1965).

(13) W. I. Bailey, Jr., D. M. Collins, F. A. Cotton, J. C. Baldwin, and W. C. Kaska, *J. Organomet. Chem.*, **165**, 373 (1979).

(14) R. E. Ginsburg, L. M. Cirjak, and L. F. Dahl, *J. Chem. Soc., Chem. Commun.*, 468 (1979).

(15) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 61.

reflections yielded an orientation matrix, from which unit cell parameters with their associated standard errors were obtained and angle settings for all reflections were generated. ω scans of a few reflections showed well-defined peaks. The θ–2θ step scan technique was used to measure intensities with a variable scan speed in 2θ of 4.00–24.00°/min from 1.00° below $K\alpha_1$ to 1.00° above $K\alpha_2$; the actual scan speed for each reflection was computer-determined from an initial 3-s scan over the central one-third of the peak. No background counting was done due to the availability of a data reduction program[16a] which performs a profile analysis on the step scans. Two standard reflections were remeasured after every 48 data, which were collected in the reciprocal lattice octants hkl and $hk\bar{l}$ for $3.00° \leq 2\theta \leq 70.00°$ and were sampled only once. Crystal movement during data collection required crystal realignment and calculation of a new orientation matrix before resumption. A small but definite sublimation of the crystal in the capillary during X-ray exposure necessitated a decay correction (<7%) of the intensities.

On the basis of a modification of the Lehmann–Larsen algorithm, data reduction[16a] yielded structure factors, F_{obsd}, and their estimated errors, $\sigma(F_{obsd})$, which were corrected for Lorentz–polarization effects including polarization due to the monochromator crystal treated as half-mosiac and half-ideal.[17] Observed systematic absences for $\{0k0\}$ data with $k = 2n + 1$ and for $\{h0l\}$ data with $h + l = 2n + 1$ uniquely defined the space group as $P2_1/n$. An absorption correction[16b] was made, on the basis of a calculated linear absorption coefficient, μ, of 13.76 cm^{-1} for Mo $K\bar{\alpha}$ radiation.[18] The crystal, defined by the faces ($\bar{1}01$), (011), ($10\bar{1}$), ($0\bar{1}\bar{1}$), ($0\bar{1}1$), and ($01\bar{1}$), produced estimated absorption coefficients which ranged between 0.425 and 0.628. The data were sorted, merged, and decay-corrected[16c] to yield 2509 independent reflections with $I \geq 2\sigma(I)$.

Unit Cell Data. The measured lattice constants and estimated standard deviations for the monoclinic cell at ca. 22 °C are a = 7.507 (2) Å, b = 10.770 (2) Å, c = 15.288 (4) Å, and β = 97.92 (2)°. The unit cell volume of 1224.1 (5) Å^3 gave rise to a calculated density of 1.357 g/cm^3 for Z = 4 and fw = 250.18. The total number of electrons in the unit cell, $F(000)$, are 520. The structural analysis required the location of one independent monomeric unit consisting of 1 cobalt, 2 oxygen, 12 carbon, and 15 hydrogen atoms, each occupying the fourfold set of general equivalent positions: $\pm(x, y, z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$.

Structural Determination and Refinement. The atomic scattering factor tables for the nonhydrogen neutral atoms were generated with the nine-parameter equation given by Cromer and Mann,[19a] while those for the hydrogen atoms are from Stewart, Davidson, and Simpson.[19b] Anomalous dispersion corrections (Mo $K\alpha$ radiation) were made for Co ($\Delta f'$ = 0.299, $\Delta f''$ = 0.973), O ($\Delta f'$ = 0.008, $\Delta f''$ = 0.006), and C ($\Delta f'$ = 0.002, $\Delta f''$ = 0.002).[19c]

The crystal structure was determined from an analysis of a Patterson synthesis,[16d] followed by successive Fourier maps which located all 15 methyl hydrogen atoms. Least-squares refinement[16e,20] with varying positional and anisotropic thermal parameters for the nonhydrogen atoms and varying positional and isotropic thermal parameters for the hydrogen atoms proceeded smoothly, and the final, full-matrix

Table I. Atomic Parameters for Co[η^5-$C_5(CH_3)_5$]$(CO)_2$[a]

A. Positional Parameters

atom	x	y	z
Co	0.16295 (7)	0.20711 (5)	0.11562 (3)
O(1)	−0.0548 (6)	0.1623 (5)	0.2519 (3)
O(2)	−0.0990 (6)	0.3659 (5)	0.0180 (3)
C(1)	0.0326 (6)	0.1796 (4)	0.1980 (3)
C(2)	0.0050 (7)	0.3036 (5)	0.0568 (3)
C(11)	0.4396 (5)	0.2473 (4)	0.1341 (3)
C(12)	0.4049 (5)	0.1337 (4)	0.1749 (3)
C(13)	0.3246 (5)	0.0496 (4)	0.1071 (3)
C(14)	0.3046 (5)	0.1120 (4)	0.0266 (3)
C(15)	0.3724 (5)	0.2366 (4)	0.0439 (3)
C(21)	0.5366 (9)	0.3590 (7)	0.1773 (5)
C(22)	0.4605 (10)	0.1014 (10)	0.2700 (5)
C(23)	0.2799 (10)	−0.0846 (5)	0.1205 (7)
C(24)	0.2356 (8)	0.0599 (7)	−0.0623 (4)
C(25)	0.3841 (9)	0.3347 (6)	−0.0256 (4)
H(11)	0.664 (10)	0.360 (8)	0.171 (5)
H(12)	0.521 (8)	0.354 (7)	0.238 (5)
H(13)	0.480 (12)	0.441 (10)	0.140 (6)
H(21)	0.565 (8)	0.064 (6)	0.273 (4)
H(22)	0.382 (7)	0.030 (6)	0.285 (4)
H(23)	0.453 (11)	0.161 (8)	0.311 (5)
H(31)	0.373 (9)	−0.128 (7)	0.126 (4)
H(32)	0.190 (11)	−0.117 (9)	0.076 (6)
H(33)	0.265 (11)	−0.115 (9)	0.169 (6)
H(41)	0.323 (7)	0.019 (5)	−0.084 (4)
H(42)	0.186 (8)	0.129 (7)	−0.101 (4)
H(43)	0.140 (9)	0.007 (6)	−0.061 (4)
H(51)	0.485 (9)	0.334 (6)	−0.051 (4)
H(52)	0.379 (8)	0.409 (7)	0.002 (4)
H(53)	0.291 (10)	0.335 (7)	−0.074 (5)

B. Anisotropic Thermal Parameters ($\times 10^4$)[b]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	164 (1)	76 (1)	42 (1)	−2 (1)	19 (1)	−5 (1)
O(1)	405 (11)	215 (6)	79 (2)	38 (7)	107 (4)	31 (3)
O(2)	326 (10)	202 (6)	117 (3)	103 (7)	22 (5)	56 (4)
C(1)	241 (10)	111 (5)	61 (3)	12 (5)	36 (4)	3 (3)
C(2)	225 (9)	120 (5)	64 (3)	25 (6)	36 (4)	6 (3)
C(11)	167 (7)	96 (4)	52 (2)	−23 (4)	10 (3)	−13 (2)
C(12)	174 (7)	120 (5)	47 (2)	12 (5)	7 (3)	11 (3)
C(13)	161 (7)	77 (3)	68 (3)	6 (4)	25 (3)	6 (2)
C(14)	153 (7)	94 (4)	47 (2)	5 (4)	19 (3)	−15 (2)
C(15)	169 (7)	84 (4)	46 (2)	−1 (4)	22 (3)	2 (2)
C(21)	269 (13)	155 (7)	78 (4)	−73 (8)	25 (6)	−40 (4)
C(22)	292 (15)	230 (11)	57 (3)	41 (11)	12 (5)	40 (5)
C(23)	266 (14)	77 (4)	132 (6)	7 (6)	53 (7)	16 (4)
C(24)	210 (10)	175 (8)	64 (3)	−12 (7)	22 (5)	−49 (4)
C(25)	292 (13)	126 (6)	62 (3)	−2 (7)	46 (5)	20 (3)

C. Isotropic Temperature Factors

H(11)	10.9 (21)	H(21)	7.6 (16)	H(31)	8.5 (17)
H(12)	9.1 (18)	H(22)	7.3 (14)	H(32)	12.4 (26)
H(13)	14.3 (30)	H(23)	10.8 (26)	H(33)	12.3 (30)
H(41)	6.8 (13)	H(51)	8.2 (16)		
H(42)	8.5 (18)	H(52)	8.5 (18)		
H(43)	9.6 (18)	H(53)	10.5 (21)		

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] The anisotropic parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

---

(16) (a) R. W. Broach, "CARESS, a FORTRAN Program for the Computer Analysis of Step-Scan Data", Ph.D. Thesis, University of Wisconsin—Madison, 1977, Appendix I; (b) J. F. Blount, "DEAR, a FORTRAN Absorption-Correction Program", 1965 (based on the method given by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957)); (c) R. W. Broach, "QUICKSAM, a FORTRAN Program for Sorting and Merging Structure Factor Data", Ph.D. Thesis, University of Wisconsin—Madison, 1977, Appendix II; (d) J. C. Calabrese, "MAP, a FORTRAN Summation and Molecular Assemblage Program", University of Wisconsin—Madison, 1972; (e) J. C. Calabrese, "A Crystallographic Variable Matrix Least-Squares Refinement Program", University of Wisconsin—Madison, 1972; (f) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS, a FORTRAN Crystallographic Least-Squares Program", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (g) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE, a FORTRAN Crystallographic Function and Error Program", Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964; (h) D. L. Smith, "PLANES", Ph.D. Thesis, University of Wisconsin—Madison, 1962, Appendix IV; (i) C. K. Johnson, "OR TEP-II, a FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.

(17) Private communication from Dr. Arild Christensen, Syntex Analytical Instruments, Inc., 1976.

(18) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 61–2.

(19) (a) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); (c) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 149.

(20) The unweighted and weighted discrepancy factors used are $R_1(F) = [\sum ||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2(F) = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights of $w_i = 1/\sigma^2(F_o)$ assigned on the basis of the esd's[16a] of the observed structure factors.

Table II. Interatomic Distances and Bond Angles for $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$[a-d]

A. Intramolecular Distances (Å)

Co-C(1)	1.724 (5)	Co-C(11)	2.102 (4)
Co-C(2)	1.732 (5)	Co-C(12)	2.072 (4)
av	1.728	Co-C(15)	2.062 (4)
C(1)-O(1)	1.137 (6)	av	2.067
C(2)-O(2)	1.134 (6)	Co-C(13)	2.101 (4)
av	1.135	Co-C(14)	2.105 (4)
Co-Cp	1.703	av	2.103
C(11)-C(12)	1.414 (6)	C(11)-C(21)	1.510 (7)
C(15)-C(11)	1.407 (6)	C(12)-C(22)	1.498 (7)
av	1.410	C(15)-C(25)	1.510 (7)
C(12)-C(13)	1.445 (6)	av	1.504
C(14)-C(15)	1.447 (6)	C(13)-C(23)	1.504 (7)
av	1.446	C(14)-C(24)	1.495 (6)
C(13)-C(14)	1.392 (6)	av	1.500
C(21)-H(11)	0.98 (7)	C(22)-H(21)	0.88 (6)
C(21)-H(12)	0.96 (7)	C(25)-H(51)	0.90 (7)
C(21)-H(13)	1.10 (10)	av	0.89
av	1.03	C(22)-H(23)	0.91 (8)
C(23)-H(31)	0.84 (7)	C(25)-H(52)	0.91 (7)
C(24)-H(41)	0.90 (6)	av	0.91
av	0.87	C(22)-H(22)	1.01 (6)
C(23)-H(33)	0.83 (9)	C(25)-H(53)	0.94 (8)
C(24)-H(42)	1.00 (7)	av	0.98
av	0.91	H(12)···H(23)	2.44
C(23)-H(32)	0.96 (8)	H(22)···H(33)	2.43
C(24)-H(43)	0.92 (7)	H(32)···H(43)	2.47
av	0.94	H(42)···H(53)	2.37
		H(52)···H(13)	2.17

B. Intermolecular Distances (Å)[e]

O(1)···H(13)^{1}	2.91	H(23)···H(33)^{4}	2.96
O(1)···H(51)^{2}	2.98	H(23)···H(53)^{5}	2.88
C(13)···H(41)^{3}	2.81	H(31)···H(41)^{3}	2.72
H(12)···H(33)^{4}	2.75	H(31)···H(51)^{3}	2.77
H(12)···H(42)^{5}	2.59	H(32)···H(42)^{7}	2.90
H(13)···H(51)^{6}	2.81	H(32)···H(43)^{7}	2.73
H(21)···H(53)^{5}	2.91	H(52)···H(52)^{6}	2.67

C. Bond Angles (Deg)

C(1)-Co-C(2)	93.7 (2)	C(21)-C(11)-C(12)	127.1 (5)
Cp-Co-C(1)	133.2	C(21)-C(11)-C(15)	125.5 (5)
Cp-Co-C(2)	133.0	av	126.3
av	133.1	C(11)-C(12)-C(22)	125.9 (5)
Co-C(1)-O(1)	179.3 (5)	C(11)-C(15)-C(25)	125.8 (4)
Co-C(2)-O(2)	179.4 (5)	av	125.8
av	179.4	C(22)-C(12)-C(13)	125.7 (6)
C(15)-C(11)-C(12)	107.4 (4)	C(25)-C(15)-C(14)	125.0 (4)
C(11)-C(12)-C(13)	108.1 (4)	av	125.4
C(11)-C(15)-C(14)	108.9 (4)	C(12)-C(13)-C(23)	125.7 (6)
av	108.5	C(15)-C(14)-C(24)	125.7 (5)
C(12)-C(13)-C(14)	108.3 (3)	av	125.7
C(15)-C(14)-C(13)	107.1 (4)	C(23)-C(13)-C(14)	125.9 (6)
av	107.7	C(24)-C(14)-C(13)	127.1 (5)
		av	126.5

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] Averages are based on the pseudo C_s-*m* geometry. [c] Relevant distances are given out to a maximum of 3.0 Å. [d] Cp refers to the centroid of the [C(11), C(12), C(13), C(14), C(15)] ring. [e] The numerical superscripts refer to the symmetry related positions: (1) $^1/_2 - x, ^{-1}/_2 + y, ^1/_2 - z$; (2) $^{-1}/_2 + x, ^1/_2 - y, ^1/_2 + z$; (3) $1 - x, -y, -z$; (4) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$; (5) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (6) $1 - x, 1 - y, -z$; (7) $-x, -y, -z$.

Table III. Mean Planes and Interplanar Angles for $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$[a,b]

A. Planes and Perpendicular Distances (Å) of Selected Atoms from These Planes

1. Plane through Co, C(1), C(2)

$$-0.3466X - 0.7889Y - 0.5075Z + 2.9876 = 0$$

O(1)	−0.001	Cp	0.026
O(2)	0.011		

2. Plane through Co, C(1), C(2), O(1), O(2)

$$-0.3440X - 0.7909Y - 0.5062Z + 2.9886 = 0$$

Co	0.002	Cp	0.032
C(1)	0.001	O(1)	−0.000
C(2)	−0.004	O(2)	0.003

3. Plane through C(11), C(12), C(13), C(14), C(15)

$$0.9351X - 0.3159Y - 0.16082Z - 1.6327 = 0$$

Co	−1.703	Cp	0.000
C(11)	0.021	C(21)	0.131
C(12)	−0.016	C(22)	0.065
C(15)	−0.017	C(25)	0.037
C(13)	0.006	C(23)	0.089
C(14)	0.007	C(24)	0.092

B. Angles (Deg) between Normals to the Planes

	2	3
1	0.2	89.6
2		89.5

[a] The equations of the planes are given in an angstrom orthogonal coordinate system (*X, Y, Z*) which is related to the monoclinic crystallographic fractional coordinates (*x, y, z*) by the transformations $X = ax + (c \cos\beta)z$, $Y = by$, and $Z = (c \sin\beta)z$. Unit weights were used in the calculations of the planes. [b] Cp refers to the centroid of the [C(11), C(12), C(13), C(14), C(15)] ring.

least-squares cycle[16f] converged to $R_1(F) = 6.40\%$ and $R_2(F) = 6.91\%$ with no parameter shift-to-error ratio being greater than 0.02. The standard deviation in an observation of unit weight (the "goodness-of-fit"), defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.48, the number of reflections, *m*, was 2509, and the number of parameters varied in the refinement, *n*, was 196, from which $m/n = 12.8$. A final difference Fourier map, which showed the largest residual peak to be only 0.70 e/Å^3, revealed no anomalous features.

Final positional and thermal parameters are given in Table I. Interatomic distances and bond angles with estimated standard deviations (esd's)[16g] are reported in Table II. Selected least-squares planes and interplanar angles[16h] are found in Table III. Observed and calculated structure factor amplitudes are given as supplementary material.

Results and Discussion

Description of the Crystal and Molecular Structure. (Pentamethylcyclopentadienyl)cobalt dicarbonyl exists as discrete molecular species in the crystalline state. A unit cell projection down the *b* axis (Figure 1)[16i] clearly indicates the orientations of the four molecules related by crystallographic $P2_1/n$ symmetry. The smallest intermolecular H···H and H···O separations (Table II) of 2.6 and 2.9 Å, respectively (along with all other kinds of distances being >3.0 Å), show the absence of any close contacts between neighboring molecules, in accord with the premise that the crystal packing is a consequence of normal van der Waals interactions. Hence, there is no indication of any steric overcrowding of the $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ molecules which might abnormally influence its molecular geometry in the solid state.

The molecular configuration (Figure 2)[16i] consists of a cobalt atom bonded to a pentamethylcyclopentadienyl ligand and to two carbon monoxide ligands arranged symmetrically about a line defined by the cobalt and the centroid of the cyclopentadienyl ring. The molecule possesses no crystallographically imposed site symmetry in the lattice; however, the entire molecule (including hydrogen atoms) experimentally conforms to C_s-*m* geometry with the mirror plane bisecting both the $C_5(CH_3)_5$ ligand and OC–Co–CO bond angle. Hence the mirror-related distances and bond angles in Table II have been averaged accordingly.

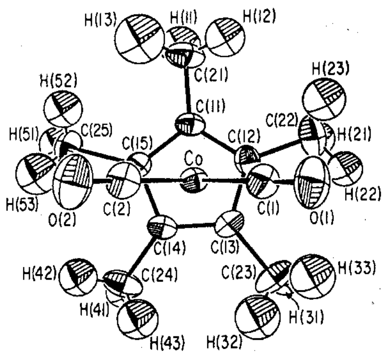


Figure 2. Molecular configuration of Co[η^5-$C_5(CH_3)_5$]$(CO)_2$, shown with 30% probability thermal ellipsoids for both the anisotropically refined nonhydrogen and isotropically refined hydrogen atoms. The pseudo bilateral mirror plane symmetry of the entire molecule is apparent.

The relatively high precision of the structural determination (coupled with no evidence of systematic error[4]) is reflected in the location and successful refinement of all of the hydrogen atoms (which, for example, resulted in a physically meaningful range of 0.83 (9)–1.10 (10) Å for the 15 independent C–H bonds) as well as in the unusually close agreement of all distances and bond angles (which possess pleasingly low esd's) not only to expected values but also to the pseudo mirror-plane symmetry of the molecule.

The Cobalt Dicarbonyl Fragment. The experimental equivalence of the two carbonyl ligands is seen from the Co–CO bond lengths of 1.724 (5) and 1.732 (5) Å and the C–O bond lengths of 1.137 (6) and 1.134 (6) Å. The C(1)–Co–C(2) bond angle of 93.7 (2)° is similar to the S–Co–S bond angle in Co(η^5-C_5H_5($S_2C_2(CN)_2$)) (93.2 (1)°)[21] and in Co(η^5-C_5H_5)($S_2C_2(CF_3)_2$) (92.2°),[22] for which a bidentate dithiolate ligand is formally substituted in place of the carbonyl ligands. Table III reveals that all atoms of the $Co(CO)_2$ fragment are coplanar within 0.005 Å.

The Pentamethylcyclopentadienyl Ligand. The relatively precise geometry of this ligand with its well-defined atomic coordinates may be largely attributed to the CH_3 substituents markedly dampening the ring thermal motion, as evidenced in Figure 2 from the small thermal ellipsoids of both the ring carbon and the methyl carbon atoms.

Figure 2 also shows that the pentamethylcyclopentadienyl ligand is symmetrically disposed relative to the planar $Co(CO)_2$ fragment such that the pseudo mirror plane bisecting the entire molecule passes through the cobalt atom, one ring carbon atom (viz., C(11)), its attached methyl carbon atom (viz., C(21)), and one of the three hydrogen atoms (viz., H(11)). Of the other four ring carbon atoms, C(12) and C(15) are mirror related as are C(13) and C(14).

The perpendicular deviations of these ring carbon atoms from their mean plane (Table III) point to a small but yet highly significant symmetrical ring distortion from planarity. Evidence for this slight ring puckering is given by these displacements, which are mirror related within experimental error, being much greater than the mean plane displacements of the atoms in the $Co(CO)_2$ fragment. Whereas the equivalent C(12) and C(15) atoms deviate from the mean plane by 0.016 and 0.017 Å, respectively, toward the cobalt atom, the C(11) atom deviates by 0.021 Å, and the equivalent C(13) and C(14) atoms by 0.006 and 0.007 Å, respectively, away from the cobalt atom.

Least-squares calculations (Table III) show that the Co-$(CO)_2$ plane intersects the mean carbocyclic ring plane at an angle of 89.5°. The resulting line of intersection passes within 0.03 Å of the ring centroid and equivalently cuts the C(12)–C(13) and C(15)–C(14) bonds. One consequence is the experimental equivalence of the corresponding Co–C(ring) distances which are consistent with the directional shifts imposed by a small bending deformation of the pentamethylcyclopentadienyl ring about the nonbonding C(12)···C(15) axis away from the cobalt atom. This is reflected in the equivalent Co–C(12) and Co–C(15) distances of 2.072 (4) and 2.062 (4) Å, respectively, being significantly shorter than the Co–C(11) distance of 2.102 (4) Å and the equivalent Co–C(13) and Co–C(14) distances of 2.101 (4) and 2.105 (4) Å, respectively. This slight ring puckering is ascribed to the electronically induced distortion of the ring due to its bonding interaction with the planar $Co(CO)_2$ fragment (vide infra).

The five methyl carbon substituents all deviate from the inner-ring plane away from the cobalt atom with a root-mean-square deviation of 0.088 Å. Interestingly, these deviations conform to mirror-plane symmetry with perpendicular displacements of 0.13 Å for C(21), 0.09 Å for both C(23) and C(24), and 0.07 and 0.04 Å for C(22) and C(25), respectively. This small but definite distortion may be ascribed (in the absence of steric effects) to a partial breakdown of the bonding orthogonality of the ring carbon atoms upon interaction of the $Co(CO)_2$ fragment with the charge density on only one side of the ring. In this connection, Bercaw and co-workers[23] found from an X-ray examination of Ti[η^5-$C_5(CH_3)_5$]$_2Cl_2$ a similar out-of-plane deformation of the methyl groups in both pentamethylcyclopentadienyl rings. In contrast to the small and relatively uniform bending of the methyl substituents observed in Co[η^5-$C_5(CH_3)_5$]$(CO)_2$, the considerably larger methyl carbon deformations in the titanium compound from the mean ring carbon planes (viz., of 0.06–0.33 Å for one ring and 0.05–0.49 Å for the other ring) could be readily attributed[23] to nonbonding intramolecular Cl···CH_3 crowding and to H_3C···CH_3 contacts between the two rings. The nonexistence of close *intramolecular* and *intermolecular* ligand···ligand separations in Co[η^5-$C_5(CH_3)_5$]$(CO)_2$ provides the basis for our conclusion that the outward bending of the methyl substituents away from the $Co(CO)_2$ fragment is due primarily to the above-mentioned electronic effect. A survey[13,14,24] of other pentamethylcyclopentadienyl–metal complexes uniformly shows this behavior to be general, with no significant exception and with root-mean-square displacements of the methyl carbons out of the least-squares planes ranging from 0.037 to 0.205 Å. Furthermore, the higher end of the range occurs in those compounds which contain intramolecular ring crowding.

The Cyclopentadienyl–$Co(CO)_2$ Interaction and Resulting Bonding Implications. The salient structural feature of Co[η^5-$C_5(CH_3)_5$]$(CO)_2$ is that this relatively precise structural determination provides unequivocal stereochemical information relating to the interaction of a cyclopentadienyl ring with a planar ML_2 fragment. The $C_5(CH_3)_5$ ring is symmetrically disposed with respect to the planar $Co(CO)_2$ fragment such that the entire molecule experimentally conforms to the C_s-m symmetry. The ring orientation relative to the $Co(CO)_2$

---

(21) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

(22) H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).

(23) T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, **102**, 457 (1975).

(24) Cf.: (a) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 572 (1971); (b) T. L. Khotsyanova and S. I. Kuznetsov, *J. Organomet. Chem.*, **57**, 155 (1973); (c) M. R. Churchill and S. Wei-Yang Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973); (d) J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, *Inorg. Chem.*, **13**, 2540 (1974); (e) R. J. Restivo, G. Ferguson, D. J. O'Sullivan, and F. J. Lalor, *ibid.*, **14**, 3046 (1975); (f) R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 8351 (1976); (g) R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, *ibid.*, **98**, 8358 (1976); (h) M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, **16**, 1137 (1977); (i) M. R. Churchill and S. A. Julis, *ibid.*, **16**, 1488 (1977).

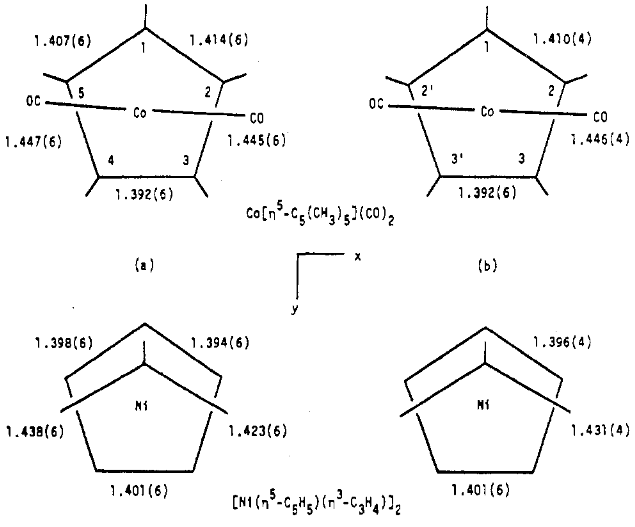


Figure 3. Schematic diagram of both $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ and half of the centrosymmetric $[Ni(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_3H_4)]_2$ species[26] showing (a) the individual C(ring)–C(ring) bond lengths and (b) the corresponding mean bond lengths in each molecule averaged under C_s-m symmetry (with the molecular mirror plane chosen perpendicular to the x axis and with the z axis directed perpendicular to the cyclopentadienyl ring).

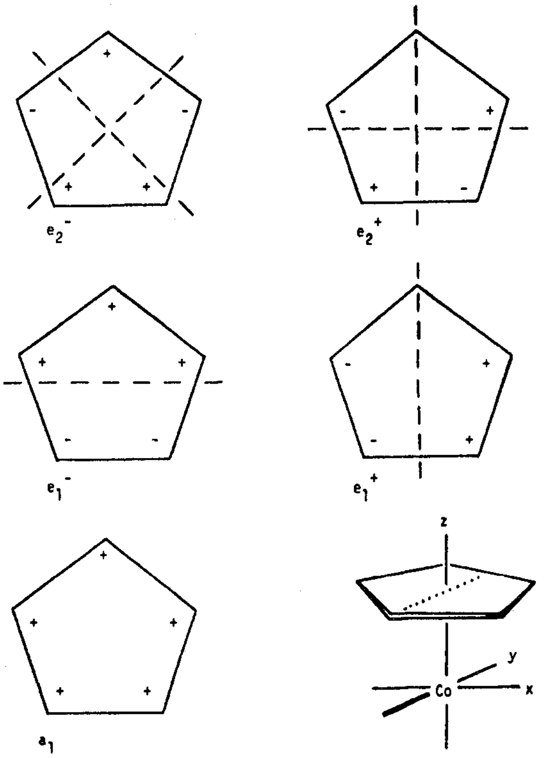


Figure 4. The five p_π ring symmetry orbitals (SO's) of the $C_5(CH_3)_5^-$ ligand under assumed C_{5v}-$5m$ symmetry. The nodal planes are indicated by dashed lines. The lower energy a_1 and doubly degenerate e_1^+ and e_1^- SO's of the "free" monoanion are filled, while the higher energy e_2^+ and e_2^- SO's are empty. On the basis of the illustrated coordinate system (with the molecular mirror defined by the yz plane), the overlaps of the interactions of these ring SO's with the appropriate Co(I) d AO's (of which all but the d_{xz} are filled) of the planar $Co(CO)_2^+$ fragment (which lies in the xz plane) are classified under their rotational symmetry as follows: $S(a_1|d_{z^2})$, σ; $S(e_1^+|d_{xz})$, π; $S(e_1^-|d_{yz})$, π; $S(e_2^+|d_{xy})$, δ; $S(e_2^-|d_{x^2-y^2})$, δ. The determined distortion toward the "allyl-ene" geometry may be attributed to the predominantly large ring-metal $S(e_1^+|d_{xz})$, π and $S(e_1^-|d_{yz})$, π interactions, by which the electron occupancy in the ring e_1^+ SO is depleted relative to that in the ring e_1^- SO. This particular electron-density localization, which is in complete accord with the observed ring deformation, results from only the *bonding* ring-metal $(e_1^+|d_{xz})$ MO being filled (i.e., due to the empty d_{xz} Co(I) AO, the corresponding *antibonding* ring-metal $(e_1^+|d_{xz})$ MO is unoccupied thereby producing a "net" π-bonding ring-metal interaction) in contrast to electron occupancy of *both* the *bonding* and *antibonding* ring-metal $(e_1^-|d_{yz})$ MO's.

fragment along with the individual and mean C(ring)–C(ring) distances are given in Figure 3. The symmetrically deformed C(ring)–C(ring) configuration consists of two adjacent intermediate C(11)–C(12) and C(11)–C(15) bonds of 1.414 (6) and 1.407 (6) Å, respectively, separated from one shorter C(13)–C(14) bond of 1.392 (6) Å by two longer C(12)–C(13) and C(15)–C(14) bonds of 1.445 (6) and 1.447 (6) Å, respectively. It is apparent that the esd's of 0.006 Å for the individual C(ring)–C(ring) bond lengths and calculated esd's of the means are sufficiently low that this observed pattern of bond-length differences in the $C_5(CH_3)_5$ ring is statistically significant. Importantly, this observed degree and kind of ring distortion (which includes the concomitantly slight ring puckering) from fivefold symmetry may readily be attributed to electronic considerations arising from interaction of a $C_5(CH_3)_5^-$ ligand with the planar $Co(CO)_2^+$ fragment, which does not possess cylindrical symmetry. On the basis of a molecular Cartesian coordinate system (given in Figure 4) with the z axis chosen along the Co–(ring centroid) line and with the orthogonal x and y axes directed within and perpendicular to, respectively, the planar $Co(CO)_2^+$ fragment, the in-plane $3d_{xz}$ and the out-of-plane $3d_{yz}$ cobalt atomic orbitals are clearly nonequivalent in energy. These nondegenerate Co(I) d AO's produce by their extensive interactions with the p_π $C_5(CH_3)_5^-$ symmetry orbitals (SO's) a splitting of the normally doubly degenerate, filled e_1 ring SO's. It is presumed from qualitative considerations (based in part upon the insight gained from the results of nonparameterized (Fenske–Hall)-type molecular orbital calculations[25] on other first-row transition-metal cyclopentadienyl complexes) that the prime electron-donor interaction of the e_1^+ ring component overlapping with the empty in-plane $3d_{xz}$ Co(I) AO should greatly diminish the e_1^+ charge density relative to the e_1^- charge density due to this other filled e_1^- component interacting with the out-of-plane filled $3d_{yz}$ Co(I) AO such that both the bonding and antibonding ring–metal $(e_1^-|d_{yz})$ MO's are occupied in contrast to electron occupancy of only the bonding ring–metal $(e_1^+|d_{xz})$ MO. In this connection, δ-type back-bonding from the filled nondegenerate $3d_{xy}$ and $3d_{x^2-y^2}$ Co(I) AO's to the normally doubly degenerate empty e_2 ring SO's (whose degeneracy is also removed by the $Co(CO)_2^+$ interaction) is reasonably presumed from energy-overlap considerations[25] to be much smaller than the π-type forward-bonding and therefore is of secondary importance in producing the observed asymmetry of the $C_5(CH_3)_5$ ring. Hence, the observed ring distortion should reflect mainly the difference in the noncylindrical charge density, comprised mainly of the e_1^- component, remaining on the ring. Of prime importance is that the observed ring distortion is completely compatible with the noncylindrical electron-density distribution of the e_1^- component, thereby giving rise to an "allyl–ene" configuration.

This observed static distortion pattern in crystalline $Co[\eta^5\text{-}C(CH_3)_5](CO)_2$ is not unlike the indicated distortions found for unsubstituted cyclopentadienyl rings in other asymmetric metal complex environments. In fact, this "allyl–ene" ring geometry was initially proposed (but not convincingly demonstrated[4]) by Mason and co-workers[2b,c] from

---

[25] Cf.: (a) D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, **98**, 50 (1976); (b) D. L. Lichtenberger, D. Sellmann, and R. F. Fenske, *J. Organomet. Chem.*, **117**, 253 (1976); (c) J. L. Petersen, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6433 (1975).

their early crystallographic studies (based upon photographic data) in 1964–1965 of various metal cyclopentadienyl complexes containing ML_n fragments.

A second statistically significant example involving a similar cyclopentadienyl ring distortion due to its interaction with a nonplanar ML_2 fragment is given by Smith,[26] who reported a relatively precise X-ray crystal structure of dicyclopentadienyl[2,2′-bis(π-allyl)]dinickel (see Figure 3). Each half of this molecule of crystallographic C_i-$\bar{1}$ site symmetry has a Ni(η^3-allyl) fragment coordinated to a cyclopentadienyl ring in such a way that the Ni(η^5-C_5H_5)(η^3-allyl) moiety experimentally conforms to C_s-m geometry. The unusually small thermal libration of the unsubstituted ring enabled Smith[26] to obtain sufficiently precise carbon coordinates that observed differences in the C(ring)–C(ring) distances (Figure 3) are statistically significant. The determined bond-length pattern shows a marked similarity to that found in Co[η^5-$C_5(CH_3)_5$]$(CO)_2$. Although the interaction of the bidentate allylic fragment with nickel atom does not produce as clear-cut a delineation of the $3d_{xz}$ and $3d_{yz}$ metal AO's relative to the cyclopentadienyl ring as that displayed by the interaction of the two carbonyl ligands with the cobalt atom, the resembling ring distortions reinforce each other in persuasively establishing to our satisfaction that a noncyclindrical ML_2 ligand can electronically generate a marked geometrical perturbation of either an unsubstituted or pentamethyl-substituted cyclopentadienyl ring. These results thereby counter previous skepticism[4] whether significant bond-length changes from regular pentagonal symmetry can occur in cyclopentadienyl rings due to localization of electron density.

The qualitative bonding model presented above to rationalize the determined bond-length trends for Co[η^5-$C_5(CH_3)_5$]$(CO)_2$ is in accord with the extended Hückel MO calculations carried out by Hofmann[27] for an assumed planar geometry of the 16-electron Mn(η^5-C_5H_5)$(CO)_2$ molecule, whose formation by photolysis of (cyclopentadienyl)manganese tricarbonyl in matrix media at 80 K was detected by Braterman and Black[28] from infrared carbonyl spectral measurements. Hofmann's calculation[27] of a Walsh-type diagram indicated a ground-state electronic stabilization of the model Mn(η^5-C_5H_5)$(CO)_2$ molecule by its transition to a pyramidal geometry in contrast to an 18-electron M(η^5-C_5H_5)L_2 system, such as Co(η^5-C_5H_5)$(CO)_2$, possessing a "planar" geometry (i.e., one with the ML_2 fragment being perpendicular to the cyclopentadienyl ring). A planar rather than pyradmidal configuration for a Co(η^5-C_5H_5)$(CO)_2$-type molecule was ascribed by Hofmann[27] to the orbital character of its HOMO, which correlates to the LUMO for an assumed "planar" Mn(η^5-C_5H_5)$(CO)_2$, being a π-type MO corresponding to the filled antibonding ring–metal ($e_1^-|d_{yz}$) combination mentioned previously.[29] Our efforts to provide an operational test of Hofmann's prediction[27] of a possible change to pyramidal geometry for a 16-electron M(η^5-C_5H_5)$(CO)_2$ system by an attempted oxidation of Co[η^5-$C_5(CH_3)_5$]$(CO)_2$ and isolation of a crystalline cationic species for X-ray diffraction characterization were unsuccessful.

Of interest is that Co(η^5-C_5H_5)$(CO)_2$ was shown from a crystallographic study[30] to behave as a strong Lewis base in its reaction with mercury(II) halide to give a 1:1 Lewis base–Lewis acid adduct, Co(η^5-C_5H_5)$(CO)_2(HgCl_2)$, in which the resultant formation of an electron-pair Co–Hg σ bond produces a "tripod" geometry for the $Co(CO)_2(HgCl_2)$ fragment. The absence of such a pyramidal geometry for a Co(η^5-C_5H_5)$(CO)_2$-type molecule per se illustrates the apparent energetic instability of a transition-metal complex containing a sterically active lone pair of metal electrons (which in this case is stabilized only via its bond formation with an appropriate Lewis acid such as $HgCl_2$) relative to the proclivity of a transition metal to prefer having the electron pair in a π- or δ-type orbital which may be stabilized by metal–ligand interactions.

Another known crystal structure of a metal cyclopentadienyl complex with a statistically significant ring deformation (which likewise is not induced by a static Jahn–Teller mechanism[31–35]) is the trans isomer of bis[dicarbonyl(π-cyclopentadienyl)iron] whose electron density was examined by Mitschler et al.,[36] from combined X-ray and neutron diffraction at liquid nitrogen temperature. Although the disposition of each of the two centrosymmetrically related cyclopentadienyl rings deviates significantly from the pseudo molecular mirror plane passing through the central $Fe_2(\mu$-$CO)_2$ core, the salient structural feature is that the determined C–C bond-length distortion of the independent ring points to a larger occupancy of the e_1^+ ring SO than of the e_1^- ring SO. This first example of a "diolefin" ring geometry (rather than an "allyl–ene" ring geometry) not only is in accord with the observed orientation

---

(26) A. E. Smith, *Inorg. Chem.*, **11**, 165 (1972).

(27) P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 537 (1977).

(28) P. S. Braterman and J. D. Black, *J. Organomet. Chem.*, **39**, C3 (1972).

(29) It should be noted that Hofmann's different labeling[27] of the LUMO for Mn(η^5-C_5H_5)$(CO)_2$ with an x–z rather than y–z atomic coordinate system stems from an arbitrary interchange of the x and y axes (see Figure 4).

(30) I. W. Nowell and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 2393 (1972).

(31) It should be emphasized that the determined bond-length variations in the cyclopentadienyl rings of the molecules discussed in this paper are *not* induced by a Jahn–Teller distortion which requires an orbitally degenerate ground state. In this connection, a different kind of deformation of the pentamethylcyclopentadienyl rings from regular pentagonal symmetry (which was described[32] as a static Jahn–Teller distortion) was recently established by Raymond, Smart, and co-workers[32] in solid Mn(η^5-C_5Me_5)$_2$ from their highly precise, comparative X-ray diffraction analyses of the closely related and highly ordered crystal structures of the bis(pentamethylcyclopentadienyl)manganese(II) and -iron(II) compounds. In contrast to the d^6 Fe(II) Fe(η^5-C_5Me_5)$_2$ molecule (of crystallographic C_{2h}-$2/m$ site symmetry) which experimentally conforms to D_{5d} symmetry, the corresponding low-spin d^5 Mn(II) molecule (of crystallographic C_i-$\bar{1}$ site symmetry), which under D_{5d} symmetry has an orbitally degenerate $^2E_{2g}$ ground state, exhibits two structural variations. The major distortion involves a statistically significant breakdown in the fivefold symmetry of the pentamethylcyclopentadienyl ring with an expanded C(3)–C(4) bond of 1.434 (2) Å relative to the other four ring-carbon bonds of lengths 1.409 (2)–1.421 (2) Å, while the marginal distortion involves a concomitantly slight slippage of the top and bottom rings in opposite directions. On the basis of EPR studies[33] of decamethylmanganocene and other related d^5 and d^7 metallocenes showing the unpaired electron in these systems to be substantially delocalized over the ring p_π orbitals, it was concluded[32] that the above-mentioned variation in ring-carbon distances may in part reflect a Jahn–Teller distortion. It should also be mentioned that calculations of the potential surface behavior of the neutral C_5H_5 radical were recently reported by Bischof[34] and subsequently by Borden and Davidson.[35] Both groups showed that a first-order Jahn–Teller distortion in the lowest doublet state of the radical (due to the triply occupied degenerate e_1 p_π MO under D_{5h} symmetry) would give rise to two considerably distorted equilibrium structures on a fivefold potential surface such that the cyclopentadienyl radical can pseudorotate from one distorted structure to another without passing through the degenerate D_{5h} configuration. By use of the MINDO/3-UHF method, Bischof[34] obtained five equivalent minima possessing the C_{2v} "diolefin" ring geometry (of $^2B_1$ state which corresponds to a dominant p_π electronic configuration $(a_1)^2(e_1^+)^2(e_1^-)^1$) and five equivalent saddle points (with an energy difference of 0.1 kcal/mol which corresponds to the interconversion barrier) possessing the C_{2v} "allyl–ene" ring geometry (of $^2A_2$ state which corresponds to a dominant p_π electronic configuration $(a_1)^2(e_1^-)^2(e_1^+)^1$). From ab initio π-space CI calculations, Borden and Davidson[35] found both the $^2B_1$ and $^2A_2$ wave functions to have essentially identical energies at their respective minimum energy geometries, which thereby suggests that the potential surface for pseudorotation in the planar cyclopentadienyl radical is essentially flat.

(32) D. P. Freyberg, J. L. Robbins, K. N. Raymond, and J. C. Smart, *J. Am. Chem. Soc.*, **101**, 892 (1979).

(33) (a) J. L. Robbins, N. M. Edelstein, S. R. Cooper, and J. L. Smart, *J. Am. Chem. Soc.*, **101**, 3853 (1979); (b) J. H. Ammeter, *J. Magn. Reson.*, **30**, 299 (1978), and references cited therein.

(34) P. Bischof, *J. Am. Chem. Soc.*, **99**, 8145 (1977).

(35) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **101**, 3771 (1979).

(36) A. Mitschler, B. Rees, and M. S. Lehmann, *J. Am. Chem. Soc.*, **100**, 3390 (1978).

of the cyclopentadienyl ring with respect to three iron-coordinated carbonyl ligands but also is in good agreement with semiempirical MO calculations carried out[36] on an idealized molecular configuration of *trans*-[$Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2$]. Hence, the existence of both kinds of possible distortions of a cyclopentadienyl ring due to lack of cylindrical symmetry has now been experimentally established.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. Co[η^5-$C_5(CH_3)_5$]$(CO)_2$, 12129-77-0.

Supplementary Material Available: A listing of the observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Synthetic, Structural, Stereochemical, and Catalytic Studies on Carbonyliridium(I) Complexes of *o*-(Diphenylphosphino)-*N*,*N*-dimethylaniline, *o*-(Diphenylphosphino)-*N*,*N*-dimethylbenzylamine, 2-(Diphenylphosphino)-*N*,*N*-dimethylethylamine, and 3-(Diphenylphosphino)-*N*,*N*-dimethylpropylamine

D. MAX ROUNDHILL,* REBECCA A. BECHTOLD, and STEPHANIE G. N. ROUNDHILL

Received May 18, 1979

The new complexes IrCl(CO)PEN and IrCl(CO)PPN have been prepared. The crystal structure of the complex IrCl(CO)PN shows a planar complex with chloride trans to the phosphine. The iridium–carbon bond (1.794 (7) Å) is short, and the iridium–phosphorus bond (2.197 (2) Å) is unusually short. These data are considered to be a consequence of the coordination of the σ-donor amine ligand. The iridium–nitrogen distance (2.180 (5) Å) is considered long. Integration of the data for ν(Ir—Cl), ν(IrC≡O), and δ(^{31}P) is used to conclude all the complexes have the same stereochemistry as IrCl(CO)PN. The complexes IrCl(CO)PN, IrCl(CO)PCN, and IrCl(CO)PEN are more effective than $IrCl(CO)(PPh_3)_2$ for the isomerization of 1-hexene under hydrogenation conditions.

Introduction

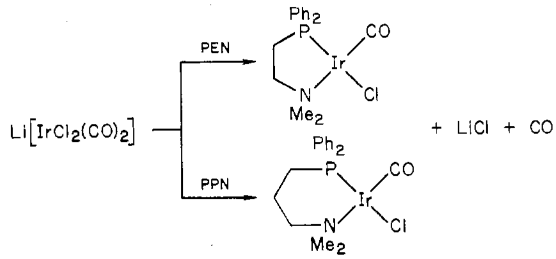
Recently we have been interested in the coordination chemistry of unsymmetrical ligands with low-valent metal centers.[1] These ligands are chosen because they have an arylphosphine at one end to stabilize the metal ion in a low oxidation state and a weakly coordinating amine or ether function at the other end which will readily be substituted by an incoming π-acceptor ligand. In our previous article[1d] we describe the preparation and chemistry of the complexes IrCl(CO)PN and IrCl(CO)PCN. We now have extended this series to the complexes IrCl(CO)PEN and IrCl(CO)PPN using the compounds 2-(diphenylphosphino)-*N*,*N*-dimethylethylamine (PEN) and 3-(diphenylphosphino)-*N*,*N*-dimethylpropylamine (PPN)[2] (Figure 1). These latter compounds are of interest to us as ligands because the fully alkylated backbone between phosphorus and nitrogen should be more flexible for allowing the amine to become distant from iridium after substitution by a π-acceptor ligand.

The compound $IrCl(CO)(PPh_3)_2$ will catalyze the hydrogenation of alkene to alkane as a homogeneous solution in dimethylformamide. The mechanistic aspects of the process have been discussed by a number of workers, and there appears to be a body of evidence supporting the view that dissociation of triphenylphosphine is a slow step in the catalytic sequence.[3] Since the dissociation of triphenylphosphine from iridium(I) is not particularly facile, this carbonyl–iridium(I) system appeared to be a good one to test our ideas on the applications of these unsymmetrical ligands to homogeneous catalysis by low-valent transition-metal compounds.

In our previous articles, the assignment of stereochemistry to the new complexes with these ligands has been rather difficult. We decided therefore to solve the structure of the complex IrCl(CO)PN, and with the stereochemistry of one complex *known*, we can use this information to deduce the stereochemistries of similar complexes by spectroscopic methods.

Results and Discussion

The complexes chlorocarbonyl(2-(diphenylphosphino)-*N*,*N*-dimethylethylamine)iridium(I), IrCl(CO)PEN, and chlorocarbonyl(3-(diphenylphosphino)-*N*,*N*-dimethylpropylamine)iridium(I), IrCl(CO)PPN, were prepared in a manner similar to IrCl(CO)PN and IrCl(CO)PCN by the addition of the appropriate ligand PEN or PPN to a solution of Li[$IrCl_2(CO)_2$] (eq 1).[4] The new complexes are air sensitive



(1)

and very soluble in a wide range of organic solvents. The complexes are primarily characterized by a carbonyl stretch band in the 1950 cm^{-1} region. The infrared and NMR spectral data for these and related compounds are collected in Tables I and II. Other preparative routes beginning with [IrCl-

---

(1) (a) Rauchfuss, T. B.; Roundhill, D. M. *J. Organomet. Chem.* **1973**, *59*, C30–2. (b) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098–105. (c) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652–6. (d) Rauchfuss, T. B.; Clements, J. L.; Agnew, S. F.; Roundhill, D. M. *Inorg. Chem.* **1977**, *16*, 775–8.

(2) (a) Knebel, W. I.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 713–6. (b) Taylor, R. C.; Walters, D. B. *Tetrahedron Lett.* **1972**, 63–6.

(3) (a) Strohmeier, W.; Onoda, T. *Z. Natuforsch B.* **1969**, *24*, 1217–9. (b) James, B. R.; Memon, N. A. *Can. J. Chem.* **1968**, *46*, 217–23. (c) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; Chapter XII.

(4) Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, 433–6.

0020-1669/80/1319-0284$01.00/0