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# CRYSTAL AND MOLECULAR STRUCTURE OF (π-CYCLOPENTADIENYL)-(π-CYCLOBUTADIENE)COBALT

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## Summary

The crystal and molecular structure of (π-cyclopentadienyl)(π-cyclobutadiene)-cobalt, $(C_5H_5)(C_4H_4)Co$, has been determined by single crystal X-ray diffraction techniques using three-dimensional data gathered at ca. −35°C by counter methods. Crystals are yellow-orange of irregular shape and of orthorhombic space group *Pnma* with lattice parameters (at ca. −35°C) $a$ = 10.162(2), $b$ = 9.041(2), and $c$ = 7.672(2) Å for a unit cell with four molecules of $(C_5H_5)(C_4H_4)Co$. The molecule consists of a Co atom sandwiched between the π-bonding cyclopentadienyl and cyclobutadiene ligands. A crystallographic mirror plane passes through the molecule and contains two carbons of the $C_4H_4$ moiety resulting in an ordered structure with $C_s$ symmetry. Full-matrix least-squares refinement has converged with a $R$ index (on $F$) of 0.025 for all 681 symmetry-independent reflections examined within the Mo-$K_\alpha$ shell defined by 4° < $2\theta$ < 50°.

## Introduction

Synthesis of a stable organocobalt sandwich compound with the cyclopentadienyl ligand and the tetraphenyl-substituted cyclobutadiene ring was reported in 1961 [1]. Following that paper, accounts of the preparation and properties of several other analogous cobalt sandwich complexes, all possessing substituted cyclobutadiene ligands, appeared [2,3]. Successful synthesis of the unsubstituted parent complex (π-cyclopentadienyl)(π-cyclobutadiene)cobalt, $(C_5H_5)$-$(C_4H_4)Co$, was eventually achieved by Amiet and Pettit in 1968 [4].

Following the isolation of crystals of $(C_5H_5)(C_4H_4)Co$, a single crystal X-ray diffraction study of this novel species was attempted in our laboratory. Unfortunately rapid sublimation or decomposition of this material during data collection under conventional laboratory conditions precluded the success of these efforts at that time (ca. 1968). With the advent of routine low-temperature inert atmosphere data gathering techniques in our laboratory, another single crystal

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X-ray diffraction study of $(C_5H_5)(C_4H_4)Co$ has been undertaken. Reported herein are the results of that endeavor.

## Experimental

An irregularly-shaped (very approximately equidimensional) yellow-orange crystal of $(C_5H_5)(C_4H_4)Co$ obtained from very slow sublimation in a vial (1 atm, −5° C, years) was attached to a glass fiber and quickly transferred to a Syntex $P2_1$ autodiffractometer. To compensate for the effects of sublimation (see Introduction) the data crystal was maintained at ca. −35° C with a stream of nitrogen during the course of all diffraction experiments. As indicated by the data collection summary in Table 1, the crystal was satisfactorily stable under these conditions.

The systematic X-ray reflection absences are consistent with two orthorhombic space groups $Pn2_1a$, acentric, point group $m2m$, and $Pnma$, centric, point group $mmm$. Since Friedel's law is violated by the anomalously scattering Co atoms of this structure, it may be possible to determine the point symmetry (and hence the true space group) by comparing appropriate sets of intensities. For example, if the point group is $m2m$ (i.e., $Pn2_1a$) $I(hkl) \neq I(hkl)$, but if the point

TABLE 1

EXPERIMENTAL SUMMARY

Crystal data for $(C_5H_5)(C_4H_4)Co$ [a]

| | |
|---|---|
| $a$ = [illegible] Å | Orthorhombic, systematic absences |
| $b$ = [illegible] Å | $h00$, $h = 2n + 1$; $0k0$, |
| $c$ = [illegible] Å | $k = 2n + 1$; $00l$, |
| $V$ = [illegible] Å$^3$ | $l = 2n + 1$; $hk0$, |
| $\rho_{calcd}$ = 1.62[illegible] g cm$^{-3}$ [b] | $h = 2n + 1$; $0kl$, |
| Formula weight 176.10 | $k + l = 2n + 1$ |

Space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62) [c]

$Z$ = 4; $F(000)$ = 360

Data collection

Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT-1 low-temperature system

Radiation: Mo-$K_\alpha$, $\lambda$ = 0.71069 Å

Mode: $\omega$-scan technique

Scan range: symmetrically over 1.0° about the $K_{\alpha_{1,2}}$ maximum

Scan rate: variable, 1.0 to 4.0°/min

Background: offset 1.0 and −1.0° in $\omega$ from $K_{\alpha_{1,2}}$ maximum

Check reflections: 4 remeasured after every 96 reflections; analysis of 32 sets of check reflections indicated a mean decline of intensity of ca. 1.5% during the 83 h of data collection. A correction for this effect was applied [d]

[illegible] reflections measured in octants $h$, $\pm k$, $\pm l$; $4° \leq 2\theta \leq 50°$

Absorption coefficient $\mu$(Mo-$K_\alpha$) = 17.2 cm$^{-1}$; no absorption correction made for rather spherical crystal used

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 30 reflections with 20° < 2θ < 30° as measured on the Syntex $P2_1$ diffractometer (Mo-$K_\alpha$ radiation). [b] Due to room temperature sublimation of $(C_5H_5)(C_4H_4)Co$, an experimental density was not determined. [c] $Pnma$ confirmed by refinement (see text). [d] Ref. 5.

group is *mmm* (i.e., *Pnma*) then these reflections are (in principle) equivalent. Examination of such sets of reflections for the hemisphere of data gathered (see Table 1) did not reveal significant variations in intensity, and hence space group *Pnma* was favored at this juncture.

The net intensities for the reflections were determined, their standard deviations were assigned (with $p = 0.02$), and Lorentz and polarization corrections were applied as described previously [6]. Using data from one octant only, the cobalt atom was located from a Patterson map at $x = 0.15$, $y = 1/4$, $z = 0.01$. A difference Fourier map phased with the Co position then revealed all the carbon atoms of the molecule. Computing the Fourier map phased only with this Co position imposes mirror symmetry (at $y = \pm 1/4$) upon the resulting map. If the space group does not possess mirror symmetry, then each carbon atom position will also appear as a mirror-related peak. Since this map exhibited only as many non-cobalt peaks as carbon atoms in the molecule, the true space group must possess mirror symmetry and hence must be *Pnma*. This is further verified by the subsequent successful refinement of the structure. (Principal computer programs used in this work are listed in ref. [6].)

Full-matrix least-squares refinement of the cobalt and carbon atom positions, first isotropically and then anisotropically, using those 591 reflections with intensities which exceeded their corresponding standard deviations by a factor of 2, converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.043$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.054$. The function minimized in refinement is $\Sigma w(|F_o| - |F_c|)^2$, where the weight $w$ is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Co, C [7], and H [8] were used, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections for anomalous dispersion were applied to the Co scattering function [9].

A difference Fourier map then readily revealed the positions of all hydrogen atoms, and incorporation of these as isotropic atoms in least-squares refinement ultimately resulted in convergence at $R = 0.028$ and $R_w = 0.034$. Inspection of the data suggested that the low order reflections were systematically affected by secondary extinction. Application of Zachariasen's correction [10] for this effect reduced both $R$ and $R_w$ to 0.023.

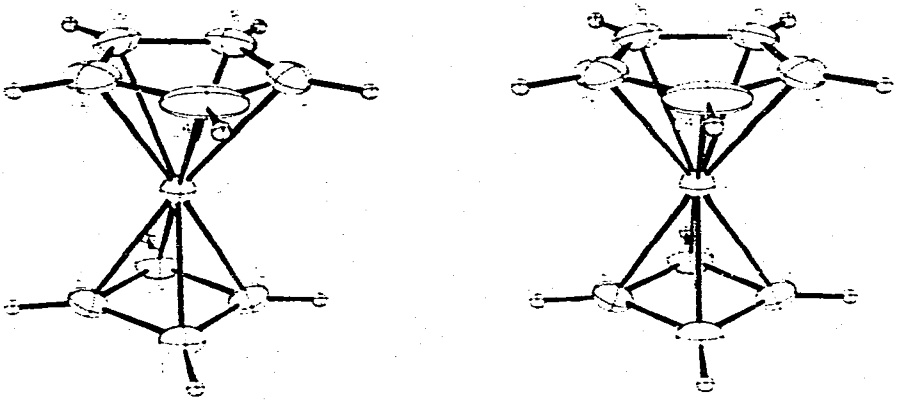

Fig. 1. A stereoview of $(C_5H_5)(C_4H_4)Co$, illustrating the atom-numbering scheme. Ellipsoids of 30% probability are shown. Hydrogen atoms are drawn as spheres of radius 0.1 Å.

TABLE 2a

FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR NONHYDROGEN ATOMS OF $(C_5H_5)(C_4H_4)Co$ [a]

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co [b] | 0.15191(3) | 0.25000 | 0.00587(4) | 407(3) | 748(4) | 767(6) | 0 | 41(4) | 0 |
| C(1) | −0.0299(2) | 0.2500 | 0.0716(3) | 43(2) | 129(4) | 111(4) | 0 | 11(3) | 0 |
| C(2) | 0.0397(2) | 0.1373(2) | 0.1627(2) | 62(2) | 106(3) | 118(3) | −12(2) | 21(2) | 19(2) |
| C(3) | 0.1097(3) | 0.2500 | 0.2550(3) | 61(3) | 151(4) | 78(4) | 0 | 10(3) | 0 |
| C(4) | 0.1789(3) | 0.2500 | −0.2557(4) | 56(3) | 393(10) | 75(4) | 0 | 14(3) | 0 |
| C(5) | 0.2364(2) | 0.1253(3) | −0.1830(3) | 89(3) | 156(4) | 223(5) | −31(3) | 72(3) | −100(4) |
| C(6) | 0.3282(2) | 0.1729(3) | −0.0657(3) | 57(2) | 153(3) | 167(4) | 32(2) | 31(2) | 34(3) |

TABLE 2b

FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS (Å$^2$) FOR HYDROGEN ATOMS OF $(C_5H_5)(C_4H_4)Co$ [a]

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H(1) [d] | 0.102(3) | 0.250 | −0.007(3) | 3.3(6) |
| H(2) | 0.036(2) | 0.034(2) | 0.167(2) | 3.4(4) |
| H(3) | 0.172(3) | 0.250 | 0.352(3) | 3.5(6) |
| H(4) [e] | 0.117 | 0.250 | −0.344 | 6.0 |
| H(5) | 0.213(3) | 0.032(3) | −0.204(3) | 6.2(7) |
| H(6) | 0.378(2) | 0.118(3) | 0.000(3) | 4.6(5) |

[a] See Fig. 1 for atom numbering scheme. Numbers in parentheses are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For atom Co the anisotropic thermal parameters are given × $10^5$. [c] Numbers in parentheses are the estimated standard deviations in the units of the last significant digits. [d] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. [e] As stated in the text, the positional and thermal parameters for H(4) are unrefined values.

The symmetry-equivalent reflections of the hemisphere of data collected (see Table 1) were then merged by taking the mean intensity $\bar{I}$ of a reflection as

$$\bar{I} = \sum_{i=1}^{n} I_i/n ,$$

and its standard deviation as

$$\sigma(\bar{I}) = [\sum_{i=1}^{n} \sigma^2(I_i)]^{1/2}/n .$$

Additional refinement now using averaged intensities for all reflections measured converged with final error indices $R$ = 0.025, $R_w$ = 0.019, and a standard deviation of an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(m - s)]^{1/2}$, of 1.93, where $m$(681) is the number of observations ($|F_o|$) and $s$(71) is the number of variables in least-squares refinement. The final value of the extinction coefficient is 4.0 (2) × $10^{-6} e^{-2}$. *

In the last cycle of least-squares refinement all shifts in nonhydrogen atom parameters were less than 0.1%, and no shift in a hydrogen atom parameter exceeded 0.1%. Hydrogen atom H(4) (See Table 2 and Fig. 1), which appeared as a very broad peak in a difference Fourier map, refined unrealistically close to carbon C(4), the atom to which it is bound. Hence in the concluding cycles of refinement, H(4) was constrained to its position estimated from the difference Fourier map. The largest residual peak on a final difference Fourier map was 0.2 $e$ Å$^{-3}$, located about midway between Co and the cyclobutadiene ring.

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* The table of structure factors has been deposited as NAPS Document No. 02774 (5 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

## Discussion

Figure 1 provides a stereoview of one molecule of $(C_5H_5)(C_4H_4)Co$ and indicates the atom numbering scheme. Final atomic positional and thermal parameters with corresponding standard deviations as estimated from the least-squares inverse matrix are given in Table 2. Bond lengths and bond angles are presented in Tables 3 and 4.

The crystal structure consists of discrete molecules of $(C_5H_5)(C_4H_4)Co$ which may be regarded as composed of two organometallic fragments, one of $C_{4v}$ symmetry (i.e., $(C_4H_4)Co$) and the other of $C_{5v}$ symmetry (i.e., $(C_5H_5)Co$), joined at Co. Atoms Co, C(1), C(3), C(4), H(1), H(3) and H(4) (see Fig. 1 and 2 ) lie on a crystallographic mirror plane, and hence the molecule has $C_s$ (*m*) symmetry. The angle between the best planes defined by the carbon atoms of each ring is 0.9°, so that the two rings are virtually parallel.

Cobalt is bound symmetrically to each ring. The Co—C(Cp) distances given in Table 3 average 2.036(9) Å *, and correspond to typical Co—cyclopentadienyl $\pi$ interactions in diamagnetic complexes. For example, the mean Co—C(Cp) bond length in $(C_5H_5)(B_{10}C_2H_{12})Co$ is 2.038 Å [12], and those in the *cis* and *trans* isomers of $(C_5H_5)\{(C_6H_5)[Si(CH_3)_3]C_2\}_2Co$ are 2.05 Å [13,14]. However, the mean Co—C(Cp) distance in the paramagnetic complex cobaltocene is longer, 2.096(8) Å [15]. The Co—C(Cb) bonds (Cb = cyclobutadiene) which are characteristically shorter than Co—C(Cp) bonds, average 1.964(2) Å in $(C_5H_5)(C_4H_4)Co$, a value which may be compared to the mean bond length of 1.982(15) Å found in the *trans* isomer of $(C_5H_5)\{(C_6H_5)[Si(CH_3)_3]C_2\}_2Co$ [14]. A significant difference, similar to that reported in ref. 14, is observed for the two Co to ring centroid distances in $(C_5H_5)(C_4H_4)Co$: Co to Cp = 1.660(1) Å, Co to Cb = 1.681(1) Å. Comparison of these distances and other selected aspects of the molecular geometry of $(C_5H_5)(C_4H_4)Co$ to equivalent features of some analogous complexes is provided in Table 5.

The C—C(Cp) bond lengths range from 1.384(3) to 1.393(3) Å and average

TABLE 3

BOND LENGTHS (Å) FOR $(C_5H_5)(C_4H_4)Co$ [a]

| | | | |
|---|---|---|---|
| Co—C(1) | 1.966(3) | C(5)—C(6) | 1.384(3) |
| Co—C(2) | 1.965(2) | C(6)—C(6)' [b] | 1.394(3) |
| Co—C(3) | 1.962(3) | C(1)—H(1) | 0.96(3) |
| Co—C(4) | 2.027(3) | C(2)—H(2) | 0.94(2) |
| Co—C(5) | 2.037(2) | C(3)—H(3) | 0.99(3) |
| Co—C(6) | 2.045(2) | C(4)—H(4) [c] | 0.94 |
| C(1)—C(2) | 1.434(2) | C(5)—H(5) | 0.90(2) |
| C(2)—C(3) | 1.440(2) | C(6)—H(6) | 0.88(2) |
| C(4)—C(5) | 1.393(3) | | |

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 1 for identity of atoms. [b] Coordinates of C(6)' are related to those given for C(6) in Table 2 by reflection through the mirror plane at $y$ = 1/4. [c] The coordinates of H(4) are unrefined values as stated in the text.

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* The standard deviation of a mean value is taken as $[\Sigma(x_i - \bar{x})^2/(n-1)]^{1/2}$, where $n$ is the number of observations.

TABLE 4

SELECTED BOND ANGLES (°) FOR $(C_5H_5)(C_4H_4)Co$ [a]

| | |
|---|---|
| C(2)–C(1)–C(2)' | 90.5(2) |
| C(2)–C(1)–H(1) | 134.5(1) |
| C(1)–C(2)–C(3) | 89.8(1) |
| C(1)–C(2)–H(2) | 135(1) |
| C(3)–C(2)–H(2) | 135(1) |
| C(2)–C(3)–C(2)' | 90.0(2) |
| C(2)–C(3)–H(3) | 134.8(1) |
| C(5)–C(4)–C(5)' | 107.9(2) |
| C(5)–C(4)–H(4) [b] | 126 |
| C(4)–C(5)–C(6) | 108.0(2) |
| C(4)–C(5)–H(5) | 125(2) |
| C(6)–C(5)–H(5) | 127(2) |
| C(5)–C(6)–C(6)' | 108.1(2) |
| C(5)–C(6)–H(6) | 127(2) |
| C(6)'–C(6)–H(6) | 125(2) |

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 1 for identity of the atoms. Coordinates of primed atoms are related to the coordinates of the corresponding unprimed atoms of Table 2 by reflection through the mirror plane at $y = 1/4$. [b] The coordinates of H(4) are unrefined values as stated in the text.

1.390(6) Å, a value which is significantly shorter than the distances of 1.41—1.43 Å ascribed to the C—C bonds of the cyclopentadienyl ligand as determined by electron diffraction work with ferrocene, cobaltocene and nickelocene [16], and by X-ray diffraction studies of several complexes with fixed Cp rings [15, 17 and references therein; 18]. While it is unclear why the C—C(Cp) bonds in

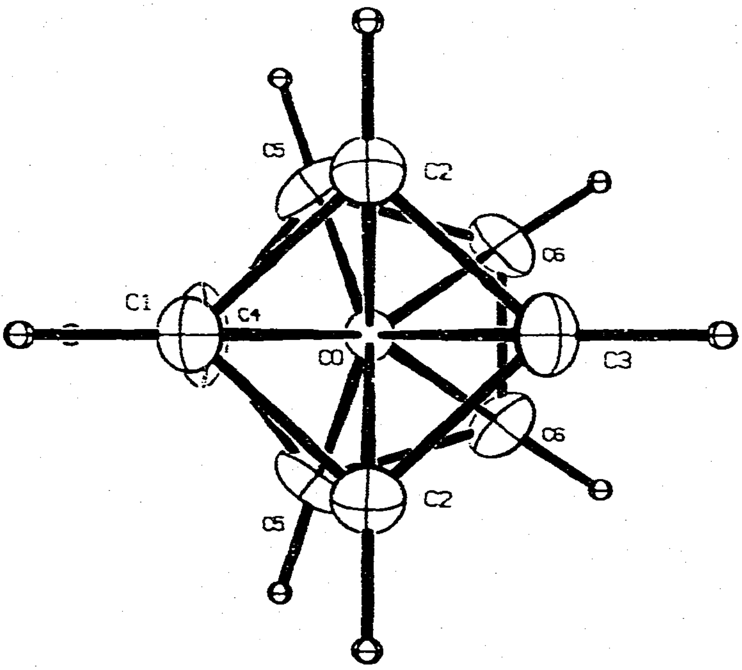

Fig. 2. A view of $(C_5H_5)(C_4H_4)Co$ normal to the cyclobutadiene ring, illustrating the relative orientations of the atoms of the two rings.

TABLE 5

COMPARISON OF SOME UNSUBSTITUTED AND SUBSTITUTED (CYCLOPENTADIENYL)(CYCLOBUTADIENE) SANDWICH COMPLEXES [a]

| | $(C_5H_5)(C_4H_4)Co$ | $(C_5H_5)\{(C_6H_5)[Si(CH_3)_3]C_2\}_2Co$ | | | $(C_5H_5)((C_6H_5)C)_4Rh$ [c] |
|---|---|---|---|---|---|
| | | *cis* isomer [b] | *trans* isomer [b] | | |
| Co—C(Cp) (Å) | 2.027(3)—2.045(2) | 2.05 | 2.05 | 2.042(3)—2.057(4) [d] | |
| Co—C(Cb) (Å) | 1.962(3)—1.966(3) | 1.97 | 1.97 | 1.968(3)—2.002(3) | |
| Co—Cp centroid (Å) | 1.660(1) | 1.68 | 1.68 | 1.673 | |
| Co—Cb centroid (Å) | 1.681(1) | 1.68 | 1.68 | 1.689 | |
| C—C(Cp) (Å) | 1.384(3)—1.394(3) | 1.40 | 1.40 | 1.373(6)—1.408(6) | 1.386(14)—1.419(10) |
| C—C—C(Cp) | 107.9(2)—108.1(2)° | — | … | 107.2(4)—109.4(4)° | 107.0(8)—109.7(8)° |
| C—C(Cb) (Å) | 1.434(2)—1.440(2) | 1.435—1.477 | 1.462—1.473 | 1.463(4)—1.471(4) | 1.463(8)—1.479(6) |
| C—C—C(Cb) | 89.9(1)—90.5(2)° | 89.3—90.7 | 88.1—92.1° | 88.1(2)—91.8(2)° | 89.7(4)—90.2(4)° |

[a] Cyclopentadienyl and cyclobutadiene moieties are abbreviated as Cp and Cb, respectively. Numbers in parentheses are the estimated standard deviations, if available, in the last significant digits of the appropriate quantities. [b] Ref. 14. [c] Ref. 11. [d] Ref. 13.

TABLE 6

SELECTED LEAST-SQUARES PLANES IN $(C_5H_5)(C_4H_4)Co$ [a]

| Atoms | Deviations (Å) from plane [b] |
|---|---|
| *Cyclobutadiene plane* $0.6943x + y - 0.7196z + 0.6113 = 0$ | |
| C(1)* | −0.001(3) |
| C(2)* | 0.001(2) |
| C(3)* | −0.001(3) |
| Co | 1.681 |
| H(1) | −0.09(3) |
| H(2) | −0.05(2) |
| H(3) | −0.08(3) |
| *Cyclopentadiene plane* $0.6833x + y - 0.7301z - 2.7116 = 0$ | |
| C(4)* | −0.002(3) |
| C(5)* | 0.002(2) |
| C(6)* | −0.001(2) |
| Co | −1.660 |
| H(4) [c] | 0.05 |
| H(5) | −0.05(3) |
| H(6) | −0.01(2) |

[a] Orthonormal (Å) coordinate system with axes *x*, *y* and *z* parallel to unit cell vectors *a*, *b* and *c*, respectively. Coordinates of atoms marked with * were used to define the planes. A negative deviation from the plane indicates that the atom with coordinates given in Table 2 lies between the plane and the origin. [b] Numbers in parentheses are the estimated standard deviations in the last significant digit. [c] The coordinates of H(4) are unrefined values as stated in the text.

$(C_5H_5)(C_4H_4)Co$ are shorter than usually reported values, it is noteworthy that the corresponding bonds in $(C_5H_5)P(C_6H_5)_3Cu$ are the same length (1.393(4) to 1.409(4) Å) [19]. Neither the internal ring angles nor the C—C—H angles of this Cp ring differ from the idealized $C_{5h}$ values of 108° and 126°, respectively. Although the Cp ring here straddles a crystallographic mirror plane, it is found to be planar, and as shown in Table 6, its hydrogen atoms apparently also lie in this plane.

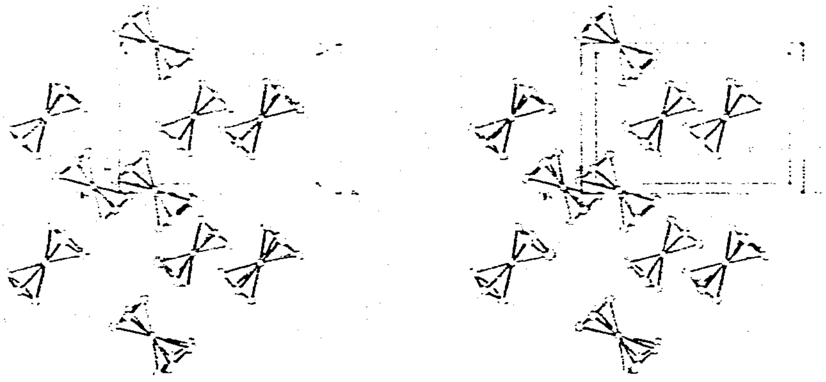

Fig. 3. A stereoview of the packing of molecules of $(C_5H_5)(C_4H_4)Co$ in the crystal. Ellipsoids of 30% probability are shown. Hydrogen atoms are not shown for sake of clarity. Each molecule is surrounded by twelve others in a nearly hexagonal closest-packed arrangement. In this view, the three molecules lying directly over the three below the central seven-plane of molecules are omitted to afford a more lucid drawing.

To our knowledge, this study has yielded the most precise geometry for an unsubstituted cyclobutadiene ligand yet reported. The ring exhibits virtually ideal $C_{4v}$ symmetry (see Table 4) with C—C(Cb) bond lengths of 1.434(2) and 1.440(2) Å, internal angles of 90° and C—C—H angles of 135° (the idealized value). For sake of comparison, the C—C(Cb) bonds in $(C_4H_4)Fe(CO)_3$ [20] and in $(C_4H_4)(C_9H_{11}O_2N)Fe$ [21] are 1.46(2) Å. Like the cyclopentadienyl ligand in $(C_5H_5)(C_4H_4)Co$, the cyclobutadiene ring possesses mirror symmetry, and within experimental error it too is planar. However, unlike this Cp ring, the Cb hydrogens appear to lie out of the carbon atom plane, at positions away from the Co atom (see Table 6).

Figure 3 illustrates the packing of molecules of $(C_5H_5)(C_4H_4)Co$ in the crystal. Each molecule is surrounded by twelve others in an approximately hexagonal closest-packed arrangement. Distances from the central Co atom to the nearest twelve Co atoms range from 5.5 to 7.7 Å.

## Acknowledgments

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