Journal of Organometallic Chemistry, 137 (1977) 91—99

CRYSTAL AND MOLECULAR STRUCTURE AT —35°C OF (π-CYCLOBUTADIENE)DICOBALT HEXACARBONYL

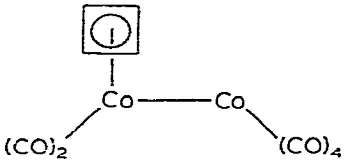
PAUL E. RILEY and RAYMOND E. DAVIS *
Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)
(Received February 8th, 1977)

Summary

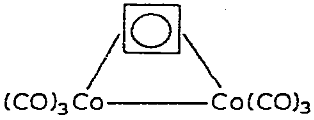
The structure of cyclobutadienedicobalt hexacarbonyl, $(C_4H_4)Co_2(CO)_6$, has been determined by single crystal X-ray diffraction techniques with data gathered at —35°C by counter methods. Crystals form as red prisms in orthorhombic space group *Pnma*, with lattice parameters (at —35°C) $a = 12.916(3)$, $b = 10.353(2)$ and $c = 9.118(3)$ Å for a unit cell with four molecules of $(C_4H_4)Co_2(CO)_6$. The molecules have rigorous C_s symmetry, with a π-cyclobutadiene ring bound to the Co atom of a $Co(CO)_2$ moiety which, in turn, is linked to a $Co(CO)_4$ fragment through the metal atoms. Apparently to decrease repulsion between the cyclobutadiene ring and the bulky $Co(CO)_4$ group, the four-membered ring is tilted, and as a consequence the Co—C_4H_4 interaction is unsymmetrical (Co—C(ring) = 1.980(3) to 2.048(4) Å). Full-matrix least-squares refinement of the structure has converged with a R index (on $|F|$) of 0.027 for 1539 symmetry-independent reflections with $I_o > 2.0\sigma(I_o)$ within the Mo-K_α shell defined by $4° < 2\theta < 60°$.

Introduction

Synthesis of the unsubstituted sandwich complex (π-cyclopentadienyl)(π-cyclobutadiene)cobalt, $(C_5H_5)(C_4H_4)Co$, the parent compound of several substituted-cyclobutadienecobalt complexes, was reported by Amiet and Pettit in 1968 [1]. (More recently, a single crystal X-ray diffraction investigation [2] of $(C_5H_5)(C_4H_4)Co$ was carried out in this laboratory to learn in detail the architecture of this interesting compound.) Based upon molecular orbital considerations, it was recently suggested [3] that the dicobalt intermediate $(C_4H_4)Co_2(CO)_6$ in the synthesis of $(C_5H_5)(C_4H_4)Co$ might not be compound I, proposed by Amiet and Pettit, but may be a novel bridging-cyclobutadiene complex, such as II, of identical stoichiometry and with very similar spectral properties. Hence, to establish the molecular structure of $(C_4H_4)Co_2(CO)_6$ we have undertaken a single crystal X-ray diffraction study of this complex, and the results of this work are reported herein.



(I)



(II)

Experimental

Crystals of the air-sensitive compound $(C_4H_4)Co_2(CO)_6$ formed slowly as red prisms by vacuum thermal gradient sublimation. A single crystal so obtained was attached to a glass fiber and quickly transferred to a Syntex $P2_1$ diffractometer where it was maintained in a stream of cold, dry nitrogen during the course of the diffraction experiments; as indicated in Table 1 the crystal was stable

TABLE 1

EXPERIMENTAL SUMMARY FOR $(C_4H_4)Co_2(CO)_6$

Crystal data [a]

$a = 12.916(3)$ Å
$b = 10.353(2)$ Å
$c = 9.118(3)$ Å
$V = 1219(1)$ Å^3
$D_c = 1.823$ g cm^{-3} [b]
Formula weight = 335.01
Space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62) [c]
$Z = 4$; $F(000) = 856e$

Orthorhombic, systematic absences:
$0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$

Data collection at —35°C

Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT - 1 inert-gas low temperature delivery system
Radiation: Mo-K_α, $\lambda = 0.71069$ Å
Mode: ω-scan technique
Scan range: symmetrically over 1.0° about $K_{\alpha_{1,2}}$ maximum
Background: offset 1.0 and —1.0° in ω from $K_{\alpha_{1,2}}$ maximum
Scan rate: variable, 1.5 to 5.0° min^{-1}
Check reflections: 4 reflections remeasured after every 96 reflections; analysis [d] of these data indicated only random fluctuation in intensity of ca. 0.2% during the 26 h of data collection with all correction factors less than 0.1σ.
2θ range: 4 to 60°
Reflections measured: 1873
Data crystal dimensions: 0.23 mm X 0.37 mm in cross section, bounded by 4 faces with edge lengths of 0.38 mm to 0.57 mm
Data crystal volume: 0.0341 mm^3
Data crystal faces: $\{100\}$, (010), (001), $(20\bar{1})$, a broken face approximately parallel to $(0\bar{1}0)$
Absorption coeff, μ(Mo-K_α): 28.4 cm^{-1}
Transmission factor range: 0.46—0.60

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 34 reflections with $12 < 2\theta < 34°$. [b] Due to the air-sensitivity of this compound an experimental density was not determined. [c] $Pnma$ confirmed by successful structure refinement (see text). [d] Ref. 4.

under these conditions. Preliminary examination of the crystal suggested the orthorhombic symmetry of either space group $Pn2_1a$ (no. 33) or $Pnma$ (no. 62). Crystal data and data collection details for $(C_4H_4)Co_2(CO)_6$ are summarized in Table 1. The measured intensities were reduced, corrected for absorption and assigned standard deviations (with $p = 0.02$) as described previously [5].

Solution and refinement of the structure

The positions of the two cobalt atoms were located from a Patterson map at (0.240, 1/4, 0.020) and (0.150, 1/4, 0.290), while the positions of the remaining nonhydrogen atoms were readily determined from the ensuing difference Fourier map phased with these heavy atom coordinates. Since $y = 1/4$ for the Co atoms, the resulting Fourier map would have mirror symmetry, even if the space group were $Pn2_1a$. However, because this map exhibited only as many (non-cobalt) peaks as carbon and oxygen atoms in the molecule, the space group was taken as $Pnma$. This was ultimately confirmed by the successful refinement of the structure in this space group.

Full-matrix least-squares refinement of the nonhydrogen atomic positions, first isotropically and then anisotropically, using the 1539 reflections with intensities more than twice their corresponding standard deviations, converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.030$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.035$. 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 [6], C [6], O [6], and H [7] were used, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections [8] for anomalous scattering were applied to the Co scattering curve.

A difference Fourier map then revealed the positions of the cyclobutadiene hydrogen atoms at heights of 0.3 to 0.4 e Å^{-3}. On the previous difference map, the average density of a carbon atom was 4.7 e Å^{-3}. Incorporation of the hydrogens as isotropic atoms in the concluding cycles of least-squares refinement led to convergence with $R = 0.027$, $R_w = 0.026$, and a standard deviation of an observation of unit weight, $[\Sigma w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 1.47$, for $m = 1539$ observations and $s = 104$ variables. At the conclusion of refinement, a structure factor calculation with all 1873 reflections measured during data collection gave R and R_w values of 0.037 and 0.027, respectively. Examination of the data indicated no evidence of secondary extinction.

In the final cycle of least-squares refinement no nonhydrogen atom parameter shifted by more than 5% of its estimated standard deviation (e.s.d.), and no hydrogen parameter by more than 17% of its e.s.d. A final difference Fourier map was virtually featureless, the highest peak corresponding to 0.2 e Å^{-3}.

A listing of the principal computer programs used in this work is given elsewhere [5]. Table 2 presents atomic positional and thermal parameters with corresponding standard deviations as estimated from the least-squares inverse matrix. A tabulation of observed and calculated structure factor amplitudes is available *.

---

* The table of structure factors has been deposited as NAPS Document No. 03045 (10 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017 (U.S.A.). 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. Outside the U.S.A. and Canada postage is $ 3.00 for a photocopy or $ 1.00 for a fiche.

TABLE 2A. FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS (X 10^3) FOR NON-HYDROGEN ATOMS OF $(C_4H_4)Co_2(CO)_6$ [a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1) [b]	0.24053(3)	0.25	0.02201(3)	408(2)	401(2)	311(2)	0	−15(1)	0
Co(2) [b]	0.15464(3)	0.25	0.28871(3)	391(2)	444(2)	322(2)	0	−14(1)	0
C(1)	0.2341(3)	0.25	−0.1949(3)	71(3)	118(3)	34(1)	0	0(1)	0
C(2)	0.1667(2)	0.1524(3)	−0.1382(2)	90(2)	88(2)	47(1)	−14(1)	−18(1)	−14(1)
C(3)	0.1011(3)	0.25	−0.0848(4)	56(2)	137(4)	41(2)	0	−13(1)	0
C(4)	0.3237(1)	0.1170(2)	0.0649(2)	58(1)	43(1)	43(1)	−3(1)	5(1)	0(1)
C(5)	0.0810(2)	0.25	0.4553(3)	45(2)	45(1)	39(1)	0	−7(1)	0
C(6)	0.1107(2)	0.0997(2)	0.2157(2)	64(1)	66(1)	46(1)	−9(1)	7(1)	−6(1)
C(7)	0.2817(2)	0.25	0.3636(3)	51(2)	73(2)	44(1)	0	−2(1)	0
O(4)	0.3783(1)	0.0340(1)	0.0861(2)	83(1)	50(1)	76(1)	21(1)	9(1)	10(1)
O(5)	0.0338(1)	0.25	0.5599(2)	56(1)	68(1)	39(1)	0	6(1)	0
O(6)	0.0814(1)	0.0022(2)	0.1750(2)	105(2)	73(1)	80(1)	−39(1)	19(1)	−23(1)
O(7)	0.3618(2)	0.25	0.4154(3)	51(2)	155(3)	76(2)	0	−20(1)	0

TABLE 2B. FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS ($Å^2$) FOR HYDROGEN ATOMS OF $(C_4H_4)Co_2(CO)_6$ [a]

Atom [c]	X	Y	Z	U
H(1)	0.296(3)	0.25	−0.244(5)	0.10(1)
H(2)	0.165(2)	0.062(3)	−0.144(3)	0.09(1)
H(3)	0.049(3)	0.25	−0.038(5)	0.11(2)

[a] See Fig. 1 for identity of the atoms. Numbers in parentheses throughout the table are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in $Å^2$ from the general temperature factor expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For Co the anisotropic thermal parameters are given X 10^4. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

Discussion

The crystal structure of $(C_4H_4)Co_2(CO)_6$ consists of well-separated molecules of C_s (m) symmetry in which the two Co atoms, two cyclobutadiene C atoms (and accompanying H atoms) and two CO groups per molecule lie on crystallographic mirror planes at $y = \pm 1/4$. Fig. 1 provides a stereoview of one molecule of the complex and indicates the atom numbering scheme used in this paper. From Fig. 1 it is clear that the cyclobutadiene (cb) group is bonded to only one cobalt atom and that the molecule has the structure postulated by Amiet and Pettit (i.e., I; see Introduction), rather than one in which the C_4H_4 moiety bridges the metal atoms.

Tables 3 and 4 present selected interatomic distances and angles in $(C_4H_4)Co_2(CO)_6$. The coordination geometries about the two cobalt atoms differ considerably. Atom Co(1), which is bonded to the π-C_4H_4 ring, to two CO molecules and to the Co atom of the $Co(CO)_4$ fragment, exhibits no regular coordination geometry. Atom Co(2), however, which is bonded to four CO molecules and the Co atom of the $(C_4H_4)Co(CO)_2$ moiety possesses approximately trigonal bipyramidal coordination, with Co(1) and C(5) occupying axial sites (Co(1)—Co(2)—C(5) = 172°) and C(6), symmetry related C(6)′ and C(7) situated at equatorial positions (equatorial angles 116, 116, 121°). Since Co(2) lies nearly 0.3 Å from the trigonal plane of its CO ligands toward Co(1) (see Table 5), the C(5)—Co(2)—C(equatorial) angles are significantly greater than 90° (viz., 98, 98 and 99°). The bending of the equatorial CO ligands away from CO(5) may be due to greater interligand repulsion between the equatorial CO ligands and the proximate axial ligand CO(5) than between the equatorial ligands and the rather distant axial Co(1)-containing group. Somewhat analogous to this is the bending (by ~8°) of the three equatorial phosphine ligands of $CoH(N_2)(P(C_6H_5)_3)_3$ away from the axial N_2 ligand toward the smaller and apparently less repulsive axial hydrogen atom [9].

Hoffmann et al. [10] have determined from extended Hückel molecular orbital calculations that the barrier to rotation of a coordinated C_4R_4 ring about its C_4 axis in a $(C_4R_4)ML_3$ complex is very low. Accordingly, these workers conclude that there is no preferred conformation for $(C_4R_4)ML_3$ complexes and that

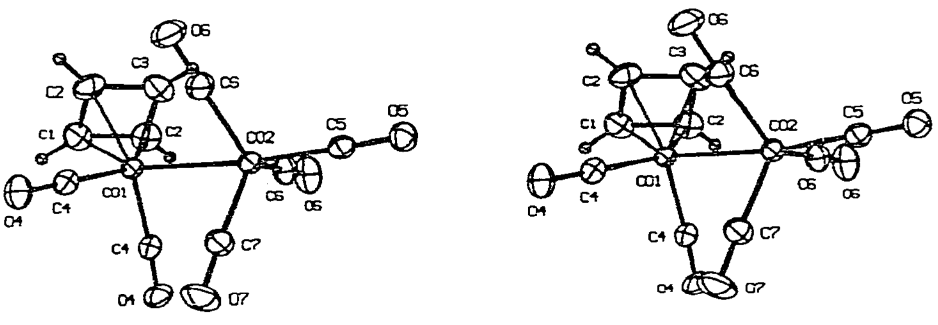


Fig. 1. Stereoview of one molecule of $(C_4H_4)Co_2(CO)_6$, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 20% probability, and hydrogen atoms as spheres of radius 0.1 Å.

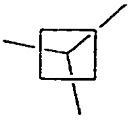
TABLE 3

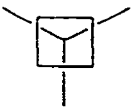
BOND LENGTHS (Å) FOR $(C_4H_4)Co_2(CO)_6$ [a]

Co(1)—Co(2)	2.673(1)	Co(2)—C(6)	1.786(2)	C(6)—O(6)	1.140(3)
Co(1)—C(1)	1.980(3)	Co(2)—C(7)	1.778(3)	C(7)—O(7)	1.138(4)
Co(1)—C(2)	2.016(3)	C(1)—C(2)	1.430(3)	C(1)—H(1)	0.92(4)
Co(1)—C(3)	2.048(4)	C(2)—C(3)	1.405(3)	C(2)—H(2)	0.94(3)
Co(1)—C(4)	1.790(2)	C(4)—O(4)	1.129(2)	C(3)—H(3)	0.80(4)
Co(2)—C(5)	1.793(2)	C(5)—O(5)	1.132(1)		

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 1 for identity of atoms.

various conformations from eclipsed (III) through staggered (IV) are possible.


(III)


(IV)

Our examination [11] of the crystal structures of several $(C_4R_4)ML_3$ and (C_4R_4)-ML_2L' species supports Hoffmann's conclusion. As shown in Fig. 2, the C(3)—H(3) and Co(1)—Co(2) bonds of $(C_4H_4)Co_2(CO)_6$ lie in the crystallographic mirror planes at $y = \pm 1/4$, and thus eclipse one another perfectly; hence these molecules have conformation III.

The metal—cyclobutadiene interaction in $(C_4H_4)Co_2(CO)_6$ is much less symmetrical (Co(1)—C distances of 1.980(3) Å, 2.016(3) Å and 2.048(4) Å to C(1), C(2) and C(3), respectively) than in most previously reported cb complexes [2,12,13], a structural feature which is undoubtedly the result of the eclipsed conformation of the molecule. In order to alleviate the repulsions due to eclips-

TABLE 4

SELECTED BOND ANGLES (°) FOR $(C_4H_4)Co_2(CO)_6$ [a]

C(1)—Co(1)—Co(2)	153.1(1)	C(6)—Co(2)—C(7)	115.9(1)
C(2)—Co(1)—Co(2)	117.6(1)	C(6)—Co(2)—C(6)′	121.3(1)
C(3)—Co(1)—Co(2)	93.9(1)	C(2)—C(1)—C(2)′	89.9(2)
C(4)—Co(1)—Co(2)	92.9(1)	H(1)—C(1)—C(2)	135.0(1)
C(1)—Co(1)—C(4)	104.1(1)	C(1)—C(2)—C(3)	89.1(2)
C(2)—Co(1)—C(4)	93.2(1)	C(1)—C(2)—H(2)	134(2)
C(3)—Co(1)—C(4)	129.2(1)	H(2)—C(2)—C(3)	136(2)
C(2)—Co(1)—C(4)′	145.9(1)	C(2)—C(3)—C(2)′	91.9(2)
C(4)—Co(1)—C(4)′	100.6(1)	C(2)—C(3)—H(3)	134.0(1)
Co(1)—Co(2)—C(5)	172.5(1)	Co(1)—C(4)—O(4)	177.0(2)
Co(1)—Co(2)—C(6)	78.0(1)	Co(2)—C(5)—O(5)	179.5(2)
Co(1)—Co(2)—C(7)	88.1(1)	Co(2)—C(6)—O(6)	177.1(2)
C(5)—Co(2)—C(6)	98.5(1)	Co(2)—C(7)—O(7)	178.1(3)
C(5)—Co(2)—C(7)	99.5(1)		

[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 $y = 1/4$.

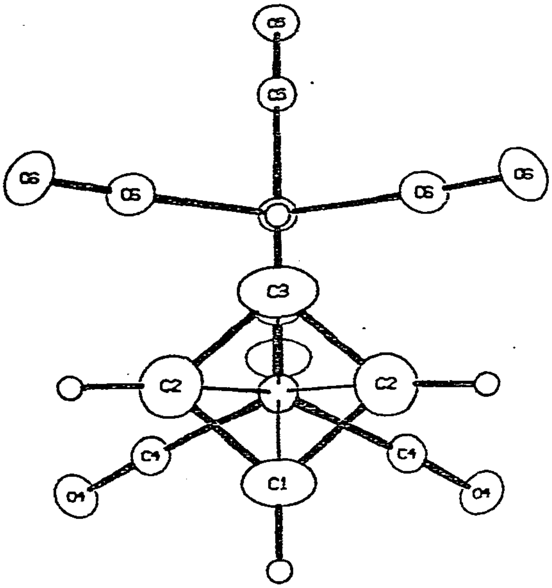


Fig. 2. A view normal to the cyclobutadiene ring, showing the orientation of the C_4H_4 ring with respect to the $(CO)_2Co(Co(CO)_4)$ moiety.

ing, the cb ring is tilted away from the bulky $Co(CO)_4$ group, toward the sterically less crowded region between ligands CO(4) and CO(4)'. Since the intermolecular contacts involving the cb ring atoms are normal (C(cb)···C > 3.50 Å, C(cb)···O ⩾ 3.22 Å, H(cb)···C ⩾ 3.24 Å, H(cb)···O ⩾ 2.66 Å), this effect cannot be atrributed to crystal packing forces.

A similar effect was noted in the structure of $[(C_4(CH_3)_4)Pt(CF_3)(P(CH_3)_2C_6H_5)_2]^+$ [14], where the π-bonded $C_4(CH_3)_4$ ring is tilted away from the bulky phosphine ligands, toward the CF_3 group. In contrast, for the more symmetrical structures of the type $(C_4R_4)ML_3$, such as $[C_4(C_6H_5)_4]Fe(CO)_3$ [12] and $\{[C_4(CH_3)_4]NiCl_2\}_2$ [13], the ML_3 fragments possess approximate C_{3v} symmetry, and the M to cb ring interactions are found to be symmetrical. That is, in $(C_4R_4)ML_3$ complexes the plane of the cb ring is not tilted with respect to the ML_3 fragment as it is in $(C_4R_4)ML_2L'$ or $(C_4R_4)MLL_2'$ complexes, where L' is a ligand which is bulkier than L, and hence the C_4 axis of the $(C_4R_4)M$ moiety is coincident with the C_3 axis of the ML_3 fragment.

The cb ring of $(C_4H_4)Co_2(CO)_6$ is planar (see Table 5). (The dihedral angle between planes C(2)—C(1)—C(2)' and C(2)—C(3)—C(2)' is 0.9°.) Although the C—C(cb) bond lengths of 1.405(3) and 1.430(3) Å appear to differ significantly, the calculated standard deviations for these values are probably artificially small, since the *y* coordinates of atoms C(1) and C(3) are fixed by symmetry. It is conceivable, however, that the asymmetry of the Co(1)—C_4H_4 interaction is at least partly responsible for this difference in bond lengths. Since the cb ring is tilted with respect to the $(CO)_2Co[Co(CO)_4]$ group (an ML_2L' group), the overlap between metal (Co(1)) and cyclobutadiene orbitals may be altered appreciably from what it would be in a symmetrical (i.e., untilted) cb complex, where the distances around the cb ring have been found to be equivalent [12,13]. In

TABLE 5

SELECTED LEAST-SQUARES PLANES FOR $(C_4H_4)Co_2(CO)_6$ [a]

Atoms	Deviations (Å) from plane [b]
C(6)—C(7)—C(6)′ plane: $0.5210X - 0.8535Z + 0.9337 = 0$ [c]	
Co(2)	−0.272(1)
O(6)	0.120(2)
O(6)′	0.120(2)
O(7)	0.137(3)
Co(1)	2.381(1)
C(5)	−2.065(2)
Cb carbon plane: $-0.5046X - 0.8634Z - 0.0047 = 0$ [c]	
C(1)	0.004(3)
C(2)	−0.004(2)
C(3)	0.004(3)
C(2)′	−0.004(2)
Co(1)	−1.746(1)
H(1)	−0.02(4)
H(2)	0.06(3)
H(3)	−0.03(4)
H(2)′	0.06(3)

[a] Orthonormal (Å) coordinate system with axes X, Y and Z parallel to unit cell vectors a, b and c, respectively. A negative deviation from the plane indicates that the atom with coordinates given in Table 2 lies between the plane and the origin. 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] Numbers in parentheses are standard deviations in the last significant digit. [c] Since this plane is parallel to the b axis by symmetry, the Y component is necessarily zero.

$(C_4R_4)ML_2L'$ complexes such as $(C_4H_4)Co_2(CO)_6$, it would be expected that the portion of the cb ring which is closer to the metal atom would interact more favorably with the metal than the portion of the ring which is more distant from the metal. Thus, the overlap between the orbitals of the $(CO)_2Co[Co(CO)_4]$ fragment and those of the C_4H_4 ring should be greater near the C(1) vertex than near the C(3) vertex in this complex. As a consequence, more electron density may be transferred from metal Co(1) to the C(1) region of the ring than to the C(3) region, resulting in a greater decrease in the bond order of the C(1)—C(2) and C(1)—C(2)′ bonds (as reflected by C—C bond elongation) than in that of the C(2)—C(3) and C(2)′—C(3) bonds. Finally, the Co(1) to ring centroid dis-

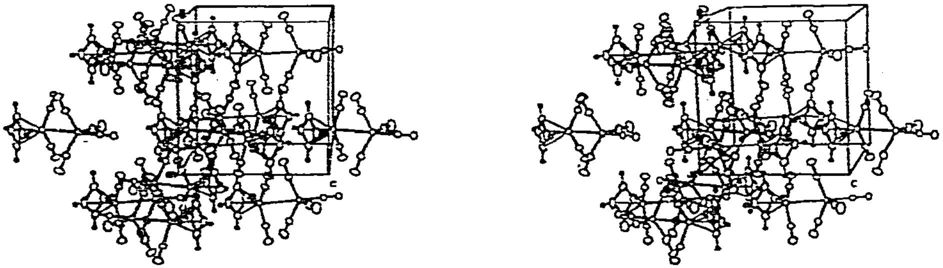


Fig. 3. Stereoview of the packing of $(C_4H_4)Co_2(CO)_6$ in the crystal. The central molecule is surrounded by the twelve closest molecules. Nonhydrogen atoms are shown as ellipsoids of 15% probability, and hydrogen atoms as spheres of radius 0.1 Å.

tance of 1.746 (1) Å in $(C_4H_4)Co_2(CO)_6$ is substantially greater than the values of 1.681 to 1.689 Å found in $(C_5H_5)(C_4H_4)Co$ and other $(C_5H_5)(C_4R_4)Co$ compounds [15], an observation which also is consistent with the asymmetric metal—cyclobutadiene interaction in $(C_4H_4)Co_2(CO)_6$.

The Co—Co bond length in $(C_4H_4)Co_2(CO)_6$ is 2.673(1) Å. This distance agrees with that reported in $\{[(C_4H_9)_3P]Co(CO)_3\}_2$ (2.66(1) Å) [16], and falls within the range of values (2.4 to 2.7 Å) [17] found in polynuclear cobalt carbonyl complexes; e.g., $Co_4(CO)_{12}$ (2.49 Å) [17] and $Co_2(CO)_8$ (2.52 Å) [18].

Figure 3 provides a stereoview of the packing of the molecules in the crystal. There is no commonly recognized arrangement of molecules (such as approximately cubic close-packed or tetragonal close-packed) in this crystal structure, and there are no unusual intermolecular contacts.

Acknowledgement

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for purchase of the Syntex $P2_1$ diffractometer (Grant No. GP-37028), to the University of Texas at Austin Computation Center and to Professor Rowland Pettit and Kevin Cann for supplying crystals of $(C_4H_4)Co_2(CO)_6$.

References

1 R.G. Amiet and R. Pettit, J. Amer. Chem. Soc., 90 (1968) 1059.
2 P.E. Riley and R.E. Davis, J. Organometal. Chem., 113 (1976) 157.
3 R. Hoffmann, personal communication to R. Pettit.
4 W.H. Henslee and R.E. Davis, Acta Crystallogr., B, 31 (1975) 1511.
5 P.E. Riley and R.E. Davis, Acta Crystallogr., B, 32 (1976) 381.
6 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
7 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
8 "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p. 149.
9 B.R. Davis, N.C. Payne and J.A. Ibers, Inorg. Chem., 8 (1969) 2719.
10 T.A. Albright, P. Hofmann and R. Hoffmann, J. Amer. Chem. Soc., in press.
11 P.E. Riley and R.E. Davis, Inorg. Chem., in press.
12 R.P. Dodge and V. Schomaker, Acta Crystallogr., 18 (1965) 614.
13 J.D. Dunitz, H.C. Mez, O.S. Mills,and H.M.M. Shearer, Helv. Chim. Acta, 45 (1962) 647.
14 D.B. Crump and N.C. Payne, Inorg. Chem., 12 (1973) 1663.
15 P.E. Riley and R.E. Davis, J. Organometal. Chem., 113 (1976) 157 (Table 5).
16 J.A. Ibers, J. Organometal. Chem., 14 (1968) 423.
17 C.H. Wei, Inorg. Chem., 8 (1969) 2384.
18 G.G. Sumner, H.P. Klug and L.E. Alexander, Acta Crystallogr., 17 (1964) 732.