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CRYSTAL STRUCTURE AT —35°C OF CARBOXYCOBALTOCENIUM HEXAFLUOROPHOSPHATE

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Summary

The crystal structure of carboxycobaltocenium hexafluorophosphate has been determined by single crystal X-ray diffraction techniques using three-dimensional data gathered at —35°C by counter methods. Bright yellow prismatic crystals are triclinic, space group $P\bar{1}$, a 7.7343(8), b 12.294(2), c 7.0316(7) Å, α 100.20(1), β 92.92(1), γ 98.91(1)°; d_m 1.93 g cm^{-3}, d_c 1.938 g cm^{-3}, with two formula weights of $[(C_5H_5)(C_5H_4COOH)Co]PF_6$ per unit cell. At convergence of full-matrix least-squares refinement, the conventional R index (on $|F|$) is 0.051 for the 3346 symmetry-independent reflections with $I_0 > 2.0\sigma(I_0)$. The crystal structure consists of hydrogen bonded dimers of $[(C_5H_5)(C_5H_4COOH)Co]^+$ ions and discrete PF_6^- anions. The cobalt ions are sandwiched between pairs of π-bonding carbocycles so as to attain a staggered ring configuration such as that observed for cobaltocene. Both rings are planar, and nearly parallel to one another (dihedral angle, 1.6°). Although the ring C—C distances in the $[(C_5H_5)(C_5H_4COOH)Co]^+$ species agree with those determined in cobaltocene, the mean Co—C(Cp) distance here (2.029(9) Å) appears to be shorter than in cobaltocene (2.096(8) Å). This difference in metal—Cp distances is rationalized in terms of the concept of imbalance in electronic configuration of the sandwich complexes.

Introduction

Recently, we completed a study of the crystal structure of (π-cyclopentadienyl)(π-cyclobutadiene)cobalt ($(C_5H_5)(C_4H_4)Co$) [1], an unsubstituted sandwich complex prepared some years earlier by Amiet and Pettit [2]. Comparison of the derived Co—C(Cp) distances (2.036(9) Å) with those found in cobaltocene (2.096(8) Å by X-ray diffraction [3] and 2.119(3) Å by gas phase electron diffraction [4]) shows the values in $(C_5H_5)(C_4H_4)Co$ to be substantially shorter, a difference readily ascribable to the change in electron distribution on the metal.

It has been shown that in the ground state, the iron atom of ferrocene has an inert gas electron configuration [5]. The other dicyclopentadienylmetal complexes of the first transition series, however, have an inappropriate number of electrons to attain a closed shell electron configuration, and hence do not contain a (net) maximum number of bonding electrons as does ferrocene [5]. Thus, it would be anticipated that the strongest M (M = 3*d* metal) to cyclopentadienyl ring interactions would occur in ferrocene, an expectation supported by comparison [3] of M—C bond lengths, the shortest being that in ferrocene.

Cobaltocene has one electron more than ferrocene, and because this electron must occupy an antibonding orbital [5], the M to ring interactions in $(C_5H_5)_2Co$ are weaker than those in $(C_5H_5)_2Fe$. However, if one C_5H_5 ring of $(C_5H_5)_2Co$ is replaced by a ligand (or ligands) such that an inert gas electron configuration is achieved about Co, then the remaining Co to C_5H_5 interaction should be strengthened. This should be reflected by a decrease in Co—C(Cp) bond length, precisely the effect observed in $(C_5H_5)(C_4H_4)Co$ and in other suitably selected $(C_5H_5)Co$-containing complexes *.

The equivalent effect should be obtained by increasing the oxidation number of the metal in the sandwich complex from +2 in cobaltocene to +3 in a cobaltocenium species. Although the crystal structures of the Co^{3+} metallocenes $[(C_5H_5)_2Co]ClO_4$ [6], $[(C_5H_5)_2Co]CoCl_4$ [7] and $[(C_5H_5)_2Co]ZnCl_4$ [7] have been reported. the results are preliminary and imprecise. Efforts in our laboratory to grow suitable crystals of a salt of $[(C_5H_5)_2Co]^+$ have yielded either very poorly formed specimens or twinned crystals. However, the production in our laboratory of excellent single crystals of the monocarboxylic acid complex, $[(C_5H_5)(C_5H_4COOH)Co]^+$, as the PF_6^- salt, afforded the opportunity for a careful study of this structural consequence of oxidation. The results of this structure determination have been discussed in brief previously [8].

Experimental

A sample of monocarboxycobaltocenium hexafluorophosphate, $[(C_5H_5)(C_5H_4COOH)Co]PF_6$ was prepared by Professor John Sheats in accordance with a previously reported method [9]. Blocky yellow crystals of this salt were grown by vapor diffusion of ether into a concentrated acetone solution. A single crystal was glued to a glass fiber and examined photographically; oscillation and Weissenberg photographs indicated triclinic symmetry. The crystal was then transferred to a Syntex $P2_1$ diffractometer which was equipped with a low-temperature inert-gas delivery system which bathed the crystal in dry, cool (—35°C) nitrogen during the course of the remaining X-ray diffraction experiments. Further examination of the crystal using the diffractometer supported the suggestion of triclinic symmetry.

Crystal data and data collection details are summarized in Table 1. The measured Bragg reflections were reduced, corrected for absorption and assigned standard deviations (with $p = 0.02$) as described elsewhere [11].

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* See compounds given in ref. 3.

TABLE 1

EXPERIMENTAL SUMMARY FOR $[(C_5H_5)(C_5H_4COOH)Co]PF_6$

Crystal data at −35°C [a]	
a	7.7343(8) Å
b	12.294(2) Å
c	7.0316(7) Å
α	100.20(1)°
β	92.92(1)°
γ	98.91(1)°
V	648.0(4) Å^3
D_m (flotation, $CCl_4/CHBr_3$)	1.93 g cm^{-3}
D_c	1.938 g cm^{-3}
Systematic absences	None
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2) [b]
Z	2
$F(000)$, electrons	186
F_w	378.11
Empirical formula	$C_{11}H_{10}CoF_6O_2P$
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)	0.71069 Å
Mode	ω scan
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—4.0 deg min^{-1}
Check reflections	4 measured after every 96 reflections; analysis [c] of these data indicated only random fluctuation in intensity with all correction factors less than 0.25 σ
2θ range	4.0—60.0°
Octants of reciprocal space examined	$\pm h$, $\pm k$, l
Total reflections measured	3765
Data crystal dimensions	0.24 × 0.27 × 0.57 mm
Data crystal volume	0.032 mm^3
Data crystal faces	(001), (010), $(0\bar{1}0)$, $(1\bar{1}0)$, $(\bar{1}10)$, $(1\bar{1}1)$, $(\bar{1}1\bar{1})$
Absorption coeff, μ(Mo-K_α)	15.8 cm^{-1}
Transmission factor range	0.64—0.76

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections of $30 < 2\theta < 36$. [b] Shown by successful refinement to be $P\bar{1}$ (see text). [c] Ref. 10.

Solution and refinement of the structure

Approximate positions of the Co and P atoms were determined from a sharpened Patterson map, and positions of the remaining nonhydrogen atoms were estimated from the ensuing heavy atom Fourier map. Full-matrix least-squares refinement of all nonhydrogen atom positions first isotropically and then anisotropically, in centrosymmetric space group $P\bar{1}$, approached convergence at $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.063$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.087$ using the 3346 data with measured intensities I_0 for which $I_0/\sigma(I_0) > 2.0$. The function minimized in refinement is $\Sigma w(|F_0| - |F_c|)^2$, where the weight w is $\sigma(|F_0|)^{-2}$, the reciprocal square of the standard deviation of each observa-

TABLE 2A

FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS (X 10^4) FOR NON-HYDROGEN ATOMS OF $[(C_5H_5)(C_5H_4COOH)Co]PF_6$ [a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co [b]	0.21052(5)	0.75341(3)	0.44322(6)	2813(22)	2275(20)	2841(22)	780(14)	355(14)	291(14)
P [b]	0.25266(12)	0.20060(8)	0.06297(13)	4089(44)	5512(51)	4070(46)	1019(37)	250(35)	771(38)
F(1)	0.0505(4)	0.1542(4)	0.0539(5)	473(17)	2048(49)	773(23)	−169(22)	64(15)	215(26)
F(2)	0.2595(5)	0.1889(4)	0.2817(4)	994(24)	1630(35)	441(15)	697(24)	150(15)	329(19)
F(3)	0.3085(6)	0.0187(3)	0.0159(7)	1623(40)	593(20)	1284(33)	317(23)	499(29)	−78(21)
F(4)	0.2376(5)	0.2051(5)	−0.1586(5)	710(21)	2395(53)	543(17)	445(26)	157(15)	596(26)
F(5)	0.2001(7)	0.3199(3)	0.1165(8)	1596(40)	758(25)	1763(45)	616(26)	870(34)	453(27)
F(6)	0.4535(4)	0.2506(4)	0.0762(5)	432(15)	1462(35)	885(23)	−88(18)	1(15)	13(23)
O(1)	0.2944(3)	0.5430(2)	0.0031(3)	397(12)	445(13)	297(11)	137(10)	−7(9)	22(10)
O(2)	0.4977(3)	0.5440(2)	0.2432(3)	357(12)	523(12)	352(12)	189(11)	1(9)	34(10)
C(1)	0.2263(4)	0.5926(2)	0.3248(4)	316(14)	244(13)	328(15)	73(11)	46(11)	27(11)
C(2)	0.2631(5)	0.6121(3)	0.5301(5)	486(19)	321(15)	338(16)	150(14)	83(14)	116(13)
C(3)	0.1120(5)	0.6445(3)	0.6148(6)	566(22)	370(17)	443(19)	109(16)	245(17)	115(15)
C(4)	−0.0149(5)	0.6476(3)	0.4634(6)	357(17)	352(17)	578(22)	56(14)	184(16)	42(15)
C(5)	0.0542(4)	0.6160(3)	0.2827(5)	270(14)	301(15)	451(18)	20(12)	36(13)	7(13)
C(6)	0.3498(4)	0.5584(2)	0.1814(4)	346(15)	249(13)	318(14)	90(11)	38(12)	21(11)
C(7)	0.1609(7)	0.8983(3)	0.3698(9)	726(32)	299(18)	893(37)	107(19)	−370(29)	123(20)
C(8)	0.1937(7)	0.9116(3)	0.5678(8)	708(29)	280(17)	748(30)	148(18)	261(25)	−15(18)
C(9)	0.3644(7)	0.8908(3)	0.6044(7)	752(31)	346(19)	639(28)	−48(19)	−324(25)	75(19)
C(10)	0.4320(6)	0.8619(4)	0.4286(10)	451(23)	360(20)	1141(47)	5(17)	209(26)	173(24)
C(11)	0.3099(9)	0.8664(4)	0.2831(7)	1308(51)	331(19)	484(24)	−77(25)	256(30)	100(18)

[a] See footnote a Table 2B.

TABLE 2B

FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS (Å^2) FOR HYDROGEN ATOMS OF [(C_5H_5)(C_5H_4COOH)Co]PF_6 [a]

Atom [c]	*X*	*Y*	*Z*	*U*
H(2)	0.392(8)	0.599(5)	0.588(8)	0.11(2)
H(3)	0.095(6)	0.655(4)	0.761(7)	0.06(1)
H(4)	−0.121(7)	0.678(5)	0.485(8)	0.08(2)
H(5)	0.001(5)	0.626(4)	0.156(6)	0.05(1)
H(7)	0.071(8)	0.894(5)	0.326(9)	0.09(2)
H(8)	0.122(7)	0.917(4)	0.652(7)	0.06(1)
H(9)	0.421(7)	0.892(5)	0.718(8)	0.08(2)
H(10)	0.530(10)	0.845(6)	0.386(11)	0.12(3)
H(11)	0.346(7)	0.839(5)	0.156(8)	0.08(2)

[a] See Fig. 2 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 and P the anisotropic thermal parameters are given × 10^5. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

tion $|F_0|$. Neutral atom scattering factors for Co, P, F, O, C [12] and H [13] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections [12] for anomalous scattering were applied to the Co and P scattering curves. A difference electron density map revealed the positions of the nine Cp ring hydrogen atoms at heights of 0.4 to 0.8 e Å^{-3}, with those of the substituted ring possessing higher densities. It should be noted that location of these hydrogen atoms confirms the initial choice of space group as $P\bar{1}$. The position of the carboxyl hydrogen atom was poorly defined with a height of 0.3 e Å^{-3}. As discussed below, this was ultimately judged to be a consequence of disorder. Continued least-squares refinement, treating the ring hydrogen atoms isotropically and omitting the acidic hydrogen atom, converged with R = 0.052 and R_w = 0.067. To take into account the secondary extinction of some low-order reflections, Zachariasen's correction [14] was included in the final cycles of refinement. At convergence, R = 0.051, R_w = 0.066 and the standard deviation of an observation of unit weight = $[\Sigma w(||F_0| - |F_c||)^2/(m - s)]^{1/2} = 4.09$, for m = 3346 observations and s = 227 variables. The value of the extinction parameter is 2.2(6) × 10^{-6} e^{-2}. A structure factor calculation with all 3765 reflections measured during data collection gave R and R_w values of 0.058 and 0.067, respectively.

The largest peaks on a final difference electron density map ranged in heights from 0.6 to 1.1 e Å^{-3}, and were associated with fluorine atoms of the PF_6^- ion. Examination of this map in the vicinity of the carboxyl group showed two peaks of height 0.3 e Å^{-3}, neither of which was situated at a geometrically reasonable location. For comparison, the carbon atoms of the heavy atom map exhibited densities of 6.4 to 9.5 e Å^{-3}. In the last cycle of refinement, all shifts in non-hydrogen atom parameters were less than 20% of a corresponding estimated standard deviation (esd), and all shifts in hydrogen atom parameters were less than 44% of an appropriate esd.

Table 2 presents the atomic positional and thermal parameters with corre-

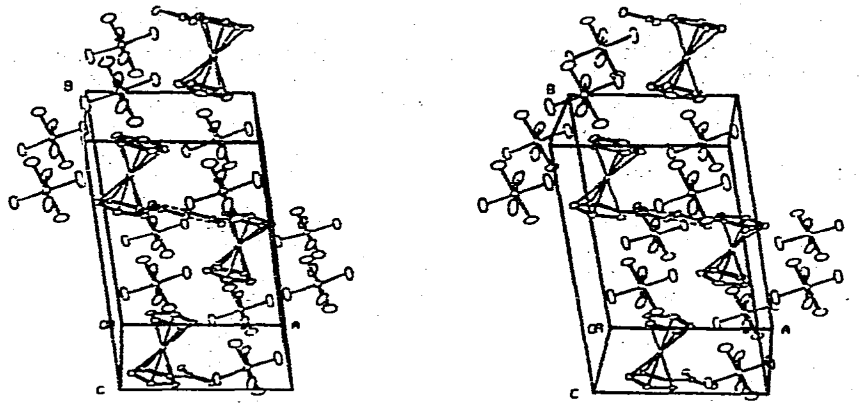

Fig. 1. A stereoscopic view of the immediate environment of a pair of hydrogen-bonded (dashed lines) cations. Each $[(C_5H_5)(C_5H_4COOH)Co]^+$ ion is surrounded by eight PF_6^- ions, four in the plane "above" a cation and four in the plane "below" it. Atoms are shown as ellipsoids of 10% probability. Hydrogen atoms have been omitted for sake of clarity.

sponding esd's as estimated from the least-squares inverse matrix for the structure of $[(C_5H_5)(C_5H_4COOH)Co]PF_6$. A tabulation of observed and calculated structure factor amplitudes is available *.

Discussion

The crystal structure of $[(C_5H_5)(C_5H_4COOH)Co]PF_6$ consists of well-separated PF_6^- ions and pairs of cations linked across the crystallographic inversion centers at 1/2, 1/2, 0 by hydrogen bonds between carboxyl groups. Although the hydrogen atoms of the carboxyl groups were not located, the intercationic O···O separations of 2.625(3) Å are substantially shorter than the Van der Waal's distance of 2.8 Å [15]. The angle between the planes of the hydrogen-bonded carboxyl groups is 0°. These parallel planes are displaced from one another by a perpendicular distance of ~0.25 Å. A similar arrangement of hydrogen-bonded dimers was found in the crystal structure of ferrocenedicarboxylic acid [16]. Despite high thermal motion of the fluorine atoms, the geometry of the PF_6^- ions is well-defined; the P—F bond lengths range from 1.568(3) to 1.574(3) Å, in agreement with values reported elsewhere [17], and the F—P—F angles deviate by no more than 4.1° from octahedral geometry. The packing of ions about a pair of hydrogen-bonded cations is shown in Fig. 1.

Figure 2 provides a stereoscopic view of the $[(C_5H_5)(C_5H_4COOH)Co]^+$ ion and illustrates the atom numbering scheme used herein. The two Cp rings are planar (see Table 3) and, as shown in Fig. 3, staggered as in the crystal structures of cobaltocene [3] and ferrocene [18]. However, unlike the situation in these latter two metallocenes, the coordinated Cp rings form an angle of 1.6°. Probably as a

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* The table of structure factors has been deposited as NAPS Document No. 03224 (19 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. Outside the U.S.A. and Canada, postage is $ 3.00 for photocopies and $ 1.00 for a fiche.

TABLE 3

CYCLOPENTADIENYL PLANES OF $[(C_5H_5)(C_5H_4COOH)Co]^+$ [a]

Atom	Deviations (Å) from plane [b]
Plane 1: $-0.2322X - 0.9727Y - 0.0066Z + 6.7253 = 0$	
C(1)*	0.008(3)
C(2)*	−0.008(4)
C(3)*	0.006(4)
C(4)*	−0.001(4)
C(5)*	−0.004(3)
C(6)	−0.013(3)
O(1)	0.026(2)
O(2)	−0.034(3)
H(2)	−0.02(6)
H(3)	0.12(5)
H(4)	−0.13(6)
H(5)	−0.19(4)
Co	−1.6358(4)
Plane 2: $-0.2242X - 0.0740Y - 0.0334Z + 10.0967 = 0$	
C(7)*	−0.006(4)
C(8)*	0.009(4)
C(9)*	−0.008(4)
C(10)*	0.005(5)
C(11)*	0.001(5)
H(7)	0.15(7)
H(8)	0.17(5)
H(9)	0.10(6)
H(10)	−0.02(8)
H(11)	0.11(6)
Co	1.6426(4)

[a] Orthonormal (Å) coordinate system with axes X, Y and Z parallel to unit cell vectors a, $c^* \times a$ and c^*. Coordinates of atoms marked with asterisks were used to define the planes. [b] Numbers in parentheses are the estimated standard deviations in the last significant digit. A negative deviation from the plane indicates that the atoms with coordinates given in Table 2 lie between the plane and the origin.

consequence of the hydrogen bonding, the carboxyl group is both twisted and bent out of the plane of its Cp ring (see Table 3 and Fig. 2), so that C(6) and O(2) are situated on the Co side of the plane and O(1) is on the opposite side of the plane.

The two C—O distances of the carboxyl group, although not equal, are similar: C(6)—O(1) = 1.276(4) Å and C(6)—O(2) = 1.252(4) Å. It would be expected, of course, that these two values would differ considerably *. As noted in the crystal structure of ferrocenedicarboxylic acid [16], the similarity in C—O bond lengths in conjunction with the inability to locate the hydroxyl hydrogen atoms (see Experimental section) strongly suggests that the cations are disordered.

Tables 4 and 5 present selected interatomic distances and angles for this structure. The Co—C(Cp) distances average ** 2.036(6) and 2.023(6) Å to the substituted and unsubstituted rings, respectively, values which are not signifi-

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* The geometry of the hydrogen bonding in twelve carboxyl groups is presented in [19].

** An average distance is given by $X = \Sigma_i^n X_i/n$, and its standard deviation by $\left[\frac{\Sigma(X_i - X)^2}{n-1}\right]^{1/2}$.

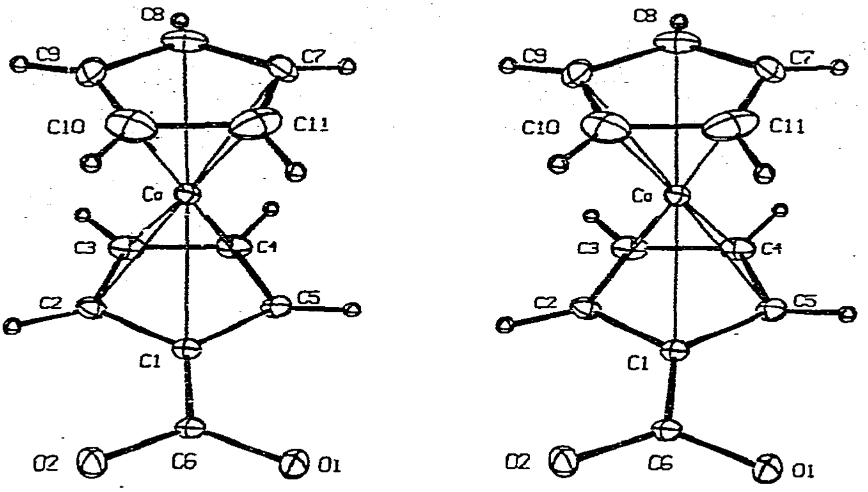

Fig. 2. Stereoscopic view of the $[(C_5H_5)(C_5H_4COOH)Co]^+$ cation, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 15% probability, and hydrogen atoms as spheres of radius 0.1 Å.

cantly different. Although the average Co—C(Cp) distance of 2.029(9) Å is considerably shorter than the average distance of 2.096(8) Å determined by the X-ray diffraction study of cobaltocene [3], it is equivalent to the Co—C(Cp) distance of 2.036(9) Å in $(C_5H_5)(C_4H_4)Co$ [1]. The reason for this variation in Co—C(Cp) distances in sandwich complexes is apparent upon examination of the electron configuration of cobaltocene.

Recent molecular orbital calculations and photoelectron spectral studies [5] have established the ground state electronic structures of several first row metallocenes. Haaland and coworkers [4,5] have introduced the concept of "electron imbalance", the number of "holes" in the bonding a_{1g} and e_{2g} orbitals together with the number of electrons in the anti-bonding e_{1g} orbitals of a metallocene. This concept has proven useful in rationalizing the observed trends in M—C(Cp)

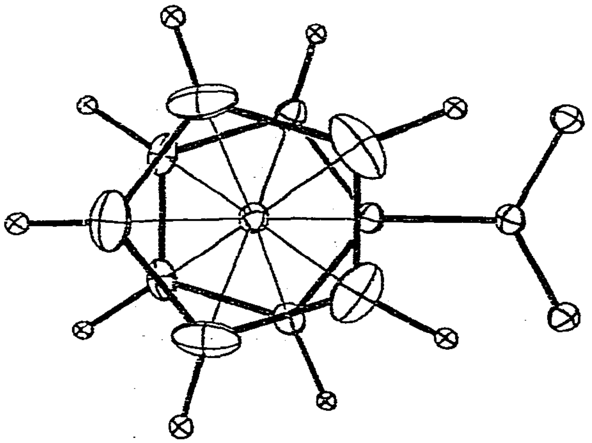

Fig. 3. A view normal to the substituted Cp ring, exhibiting the nearly perfectly staggered conformation of the two Cp rings.

TABLE 4

BOND LENGTHS (Å) FOR $[(C_5H_5)(C_5H_4COOH)Co]PF_6$ [a]

Atoms	Distance	Atoms	Distance
Co—C(1)	2.030(3)	C(7)—C(8)	1.379(8)
Co—C(2)	2.032(2)	C(8)—C(9)	1.403(7)
Co—C(3)	2.045(4)	C(9)—C(10)	1.377(8)
Co—C(4)	2.035(4)	C(10)—C(11)	1.371(8)
Co—C(5)	2.036(3)	C(2)—H(2)	1.10(6)
Co—C(7)	2.026(4)	C(3)—H(3)	1.04(5)
Co—C(8)	2.013(4)	C(4)—H(4)	0.96(6)
Co—C(9)	2.029(5)	C(5)—H(5)	0.99(4)
Co—C(10)	2.021(5)	C(7)—H(7)	0.74(6)
Co—C(11)	2.025(5)	C(8)—H(8)	0.83(5)
C(1)—C(2)	1.427(5)	C(9)—H(9)	0.89(6)
C(2)—C(3)	1.419(6)	C(10)—H(10)	0.87(7)
C(3)—C(4)	1.421(6)	C(11)—H(11)	0.97(6)
C(4)—C(5)	1.418(5)	P—F(1)	1.574(3)
C(5)—C(1)	1.432(4)	P—F(2)	1.569(3)
C(6)—C(1)	1.477(4)	P—F(3)	1.573(4)
C(6)—O(1)	1.276(4)	P—F(4)	1.568(3)
C(6)—O(2)	1.252(4)	P—F(5)	1.570(4)
		P—F(6)	1.572(3)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 2 for identity of the atoms.

distances in the metallocenes (Table 2 of ref. 4) and in understanding the differences in metallocenes (other than ferrocene) compared to those in compounds in which the inert gas configuration is maintained by ligand replacement, e.g., Cp_2Mn cf. $CpMn(CO)_3$ and Cp_2Ni cf. CpNiNO as discussed in ref. 4.

Inspection of Table 6 reveals a striking structural confirmation of this ratio-

TABLE 5

BOND ANGLES (deg) FOR $[(C_5H_5)(C_5H_4COOH)Co]^+$ [a]

Atoms	Angle	Atoms	Angle
C(5)—C(1)—C(2)	108.8(3)	C(1)—C(6)—O(2)	118.0(3)
C(5)—C(1)—C(6)	126.2(3)	O(1)—C(6)—O(2)	125.3(3)
C(6)—C(1)—C(2)	124.9(3)	C(11)—C(7)—C(8)	107.8(5)
C(1)—C(2)—C(3)	107.2(3)	C(11)—C(7)—H(7)	130(5)
C(1)—C(2)—H(2)	118(3)	H(7)—C(7)—C(8)	121(5)
H(2)—C(2)—C(3)	134(3)	C(7)—C(8)—C(9)	107.7(5)
C(2)—C(3)—C(4)	108.3(3)	C(7)—C(8)—H(8)	128(4)
C(2)—C(3)—H(3)	124(3)	H(8)—C(8)—C(9)	123(4)
H(3)—C(3)—C(4)	127(3)	C(8)—C(9)—C(10)	107.9(5)
C(3)—C(4)—C(5)	108.9(3)	C(8)—C(9)—H(9)	128(4)
C(3)—C(4)—H(4)	124(3)	H(9)—C(9)—C(10)	124(4)
H(4)—C(4)—C(5)	127(3)	C(9)—C(10)—C(11)	108.9(5)
C(4)—C(5)—C(1)	106.7(3)	C(9)—C(10)—H(10)	138(5)
C(4)—C(5)—H(5)	124(3)	H(10)—C(10)—C(11)	113(5)
H(5)—C(5)—C(1)	128(2)	C(10)—C(11)—C(7)	107.8(5)
C(1)—C(6)—O(1)	125.3(3)	C(10)—C(11)—H(11)	112(3)
		H(11)—C(11)—C(7)	140(3)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 2 for identity of the atoms.

TABLE 6

COMPARISON OF SELECTED DISTANCES (Å) OF SOME CYCLOPENTADIENYLCOBALT SANDWICH COMPLEXES [a]

Complex	Co—C(Cp)	C—C(Cp)	Co—Cp centroid	Ref.
$(C_5H_5)_2Co$ { X-ray diffraction	2.096(8)	1.41(1)	1.725	3
$(C_5H_5)_2Co$ { electron diffraction	2.119(3)	1.429(2)		4
$(C_5H_5)\{(C_6H_5)[Si(CH_3)_3]C_2\}_2Co$	2.049(7)	1.389(17)	1.673	23
$(C_5H_5)(C_4H_4)Co$	2.036(9)	1.390(6)	1.660	1
$[(C_5H_5)(C_5H_4COOH)Co]^+PF_6^-$	2.029(9)	1.423(7) [b]	1.636 [b]	This work
		1.387(18) [c]	1.643 [c]	
$(C_5H_5)(C_5H_4B_9C_2H_{11})Co$	2.027(5) [d]	1.418(9) [b]	1.641 [b]	21
		1.400(10) [c]	1.638 [c]	

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Distances involving the substituted Cp ring. [c] Distances involving the unsubstituted ring. [d] The Co—C distance for the Cp carbon bonded to the carborane cage was omitted from this calculation [21].

nale for Co sandwich complexes. Thus, the Co—C(Cp) distances for cobaltocene (one electron in an antibonding orbital) are, by Cruickshank's test [20], highly significantly longer than those for the other compounds in the table. In all of the latter compounds, the inert gas configuration is maintained either by the presence of 4-electron donor ligands in neutral complexes or by an increase in the oxidation number of the metal.

The C—C bonds in Cp_2Co average 1.41(1) Å in the crystal structure [3] and 1.429(2) Å in the gas phase (electron diffraction) structure [4]. In $[(C_5H_5)(C_5H_4COOH)Co]^+$, these distances average 1.387(18) and 1.423(7) Å for the unsubstituted and substituted rings, respectively, values which are not significantly different but which indicate the effect of hydrogen bonding upon the thermal motion of the rings. That is, the more firmly held (substituted) ring exhibits C—C distances which agree not only with those obtained from the electron diffraction study of cobaltocene but also with those found in ferrocenedicarboxylic acid, in the substituted Cp ring of $(C_5H_5)(C_5H_4B_9C_2H_{11})Co$ [21], and in other metal complexes containing constrained Cp rings [22]. As shown in Table 6, the more reliable Cp C—C bond lengths (those obtained by electron diffraction or by X-ray diffraction of firmly held rings) do not differ significantly. This observation is in agreement with the molecular orbital description [24] of Cp_2Co in which the "extra" electron (compared to Cp_2Fe) occupies an orbital (e_{1g}) which is principally antibonding between Co and the Cp rings but which apparently does not affect the Cp C—C bonding.

The equivalence of the Co—C distances for both rings of $[(C_5H_5)(C_5H_4COOH)Co]^+$ implies that, aside from diminishing the motion of the substituted ring, the electron-withdrawing carboxyl group has no apparent influence upon Co—Cp bonding.

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