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The Crystal and Molecular Structure of (η^5-Cyclopentadienyl)(η^4-2,4-dimesityl-3,5-diphenylcyclopentadienone)cobalt

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The crystal structure of (η^5-cyclopentadienyl)-(η^4-2,4-dimesityl-3,5-diphenylcyclopentadienone)-cobalt, $CoC_{40}H_{37}O$, was determined from 3385 unique reflections obtained with a computer automated diffractometer. The unit cell is triclinic with a = *8.401(3),* b = *9.339(1),* c = *20.343(3)* Å; α = *95.39(1),* β = *92.26(1),* γ = *104.93(2)°;* ρ = *1.154 g cm^{-3}, space group (assumed)* $P\bar{1}$ *and* Z = *2. Refinement of the data by the full matrix least squares procedure with anisotropic temperature factors for all non-hydrogen atoms and calculated positional and thermal parameters for hydrogen atoms resulted in a final* R *value of 0.044 (*R_w *= 0.055). The structure consists of two five membered rings π-bonded to cobalt. The cyclopentadienyl ring is planar with all five carbon atoms equidistant from the metal. However, the cyclopentadienone ring is decidedly nonplanar with the* C_1, C_2, C_3, C_4 *fragment making a dihedral angle of 10.9° with the mean plane formed by* C_1, C_5, *O,* C_4. *Torsional angles show that the substituent rings are twisted about the cyclopentadienone ring so as to minimize steric interactions. However, the short hydrogen–hydrogen interactions are sufficient to create a sizeable barrier to rotation about the mesityl–cyclopentadienone bonds.*

Introduction

The reaction of (η^5-C_5H_5)Co(CO)$_2$ with mesityl phenylacetylene in refluxing xylene was shown to produce (η^5-cyclopentadienyl)-(η^4-1,3-dimesityl-2,4-diphenylcyclobutadiene)cobalt in 48% yield and (η^5-cyclopentadienyl)-(η^4-2,4-dimesityl-3,5-diphenylcyclopentadienone)cobalt in 17% yield [1]. In the former compound, rotation about the carbon–carbon bonds linking the mesityl rings to the cyclobutadiene ring was restricted by proton–proton repulsions between the protons of the ring methyl groups and those on the five membered ring. It was, therefore, of interest to see if similar interactions occurred in the cyclopentadienone derivative.

A further incentive for determining the crystal structure derives from interest in whether or not the cyclopentadienone ring is planar and whether any steric or electronic factors could be identified as favoring the unsymmetrical 2,4 rather than the symmetrical 3,4 dimesityl derivatives [2].

Experimental

A suitable burgundy red crystal of the title complex with dimensions 0.30 × 0.33 × 0.09 mm was mounted in random orientation with the long dimension approximately parallel to the ϕ axis of a CAD 4 computer controlled 4-circle diffractometer (Enraf-Nonius). Accurate cell dimensions were determined from 25 high and moderate angle reflections which had been accurately centered. A least squares refinement yielded a triclinic cell with a = 8.401(3), b = 9.339(1), c = 20.343(3) Å; α = 95.39(1), β = 92.26(1), γ = 104.98(2)°; V = 1532(1) Å^3. Assuming Z = 2, the calculated density is ρ = 1.154 g cm^{-3} while the measured density was ρ_{obs} = 1.26 g cm^{-1} (by flotation in a benzene: chloroform mixture).

Intensity data were collected by the θ–2θ technique using monochromatized (graphite crystal) MoKα radiation (λ = 0.7107 Å) at a take-off angle of 2.8°. The scan rate was variable, ranging from 20° min^{-1} for the strongest reflections to 2° min^{-1} for the weakest. The angular scan width was also variable and amounted to 3 × (0.65 + 0.2 tan θ). Right and left backgrounds were each scanned for 25% of the total time. During data collection, three standard reflections were recorded every 175 data points and

TABLE I. Positional and Thermal Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
CO	0.17644(6)	0.02692(5)	0.30138(2)	0.00945(7)	0.00909(5)	0.00214(1)	0.0012(1)	0.00012(5)	0.00274(4)
O	−0.2250(3)	−0.0650(3)	0.2689(1)	0.0085(4)	0.0121(3)	0.00301(7)	−0.0027(6)	0.0028(3)	0.0020(3)
C1	0.0337(4)	−0.0323(4)	0.2144(2)	0.0087(5)	0.0093(4)	0.00180(9)	0.0004(8)	0.0009(4)	0.0021(3)
C2	0.1675(4)	0.0972(4)	0.2097(2)	0.0083(5)	0.0086(4)	0.00185(9)	0.0011(7)	−0.0001(4)	0.0019(3)
C3	0.1544(4)	0.2100(4)	0.2608(2)	0.0088(5)	0.0088(4)	0.00178(8)	0.0004(8)	0.0003(4)	0.0025(3)
C4	0.0043(4)	0.1556(4)	0.2934(2)	0.0089(5)	0.0090(4)	0.00175(8)	0.0014(8)	0.0007(4)	0.0027(3)
C5	−0.0845(4)	0.0098(4)	0.2590(2)	0.0091(5)	0.0093(4)	0.00202(9)	0.0013(8)	0.0004(4)	0.0032(3)
C6	0.1475(5)	−0.1062(4)	0.3771(2)	0.0175(7)	0.0145(5)	0.00299(11)	0.0049(10)	0.0008(5)	0.0070(4)
C7	0.2457(6)	0.0373(5)	0.3995(2)	0.0221(8)	0.0164(6)	0.00228(11)	0.0082(12)	−0.0011(5)	0.0043(4)
C8	0.3873(5)	0.0662(5)	0.3641(2)	0.0152(7)	0.0159(6)	0.00344(12)	0.0031(11)	−0.0049(5)	0.0050(4)
C9	0.3780(5)	−0.0597(5)	0.3192(2)	0.0149(6)	0.0180(6)	0.00434(14)	0.0146(10)	0.0023(5)	0.0073(5)
C10	0.2272(5)	−0.1661(4)	0.3276(2)	0.0199(8)	0.0104(5)	0.00403(14)	0.0080(10)	−0.0001(6)	0.0046(4)
C11	0.0033(4)	−0.1749(4)	0.1719(2)	0.0114(6)	0.0094(5)	0.00196(9)	−0.0003(8)	0.0019(4)	0.0016(3)
C12	−0.1583(5)	−0.2587(4)	0.1528(2)	0.0126(6)	0.0112(5)	0.00257(11)	0.0005(9)	0.0001(4)	0.0007(4)
C13	−0.1886(6)	−0.3915(5)	0.1127(2)	0.0198(8)	0.0123(6)	0.00322(13)	−0.0016(12)	−0.0014(6)	−0.0006(5)
C14	−0.0603(6)	−0.4442(5)	0.0902(2)	0.0281(10)	0.0106(6)	0.00267(12)	−0.0003(13)	0.0028(6)	−0.0003(4)
C15	0.0987(6)	−0.3642(5)	0.1092(2)	0.0223(8)	0.0134(6)	0.00347(13)	0.0086(11)	0.0071(5)	0.0008(5)
C16	0.1306(5)	−0.2318(4)	0.1495(2)	0.0130(6)	0.0120(5)	0.00317(12)	0.0007(10)	0.0029(5)	0.0002(4)
C21	0.2676(4)	0.1239(4)	0.1500(2)	0.0103(5)	0.0091(4)	0.00210(9)	0.0014(8)	0.0026(4)	0.0018(3)
C22	0.1768(5)	0.1382(4)	0.0922(2)	0.0130(6)	0.0106(5)	0.00212(9)	0.0018(9)	0.0022(4)	0.0018(4)
C22′	−0.0055(5)	0.1301(5)	0.0908(2)	0.0135(6)	0.0169(6)	0.00267(11)	0.0065(10)	0.0006(5)	0.0042(4)
C23	0.2586(5)	0.1695(5)	0.0354(2)	0.0178(7)	0.0171(6)	0.00210(10)	0.0044(11)	0.0024(5)	0.0027(4)
C24	0.4245(5)	0.1878(5)	0.0326(2)	0.0207(8)	0.0186(7)	0.00291(12)	0.0096(12)	0.0073(5)	0.0043(5)
C24′	0.5130(7)	0.2220(7)	−0.0295(3)	0.0321(11)	0.0357(12)	0.00409(14)	0.0175(19)	0.0138(6)	0.0096(7)
C25	0.5120(5)	0.1787(5)	0.0895(2)	0.0117(6)	0.0194(7)	0.00448(14)	0.0087(10)	0.0080(5)	0.0060(5)
C26	0.4381(5)	0.1503(4)	0.1492(2)	0.0110(6)	0.0148(6)	0.00313(12)	0.0043(10)	0.0028(5)	0.0039(4)
C26′	0.5479(5)	0.1554(7)	0.2092(3)	0.0092(7)	0.0372(11)	0.00540(17)	0.0013(15)	0.0025(6)	0.0137(7)
C31	0.2758(4)	0.3576(4)	0.2754(2)	0.0085(5)	0.0078(4)	0.00279(10)	0.003(8)	0.0009(4)	0.0018(4)
C32	0.3427(5)	0.4391(4)	0.2245(2)	0.0189(7)	0.0103(5)	0.00332(12)	0.0007(10)	0.0058(5)	0.0032(4)
C33	0.4616(5)	0.5739(5)	0.2396(3)	0.0182(7)	0.0099(5)	0.00575(16)	0.0000(11)	0.0101(6)	0.0055(5)
C34	0.5113(5)	0.6304(4)	0.3033(3)	0.0110(7)	0.0080(5)	0.00675(20)	−0.0010(10)	0.0003(6)	0.0022(5)
C35	0.4417(5)	0.5541(5)	0.3536(2)	0.0175(8)	0.0105(5)	0.00453(16)	0.0010(11)	−0.0061(6)	−0.0011(5)
C36	0.3248(5)	0.4172(4)	0.3400(2)	0.0135(6)	0.0107(5)	0.00277(12)	0.0027(9)	−0.0005(5)	−0.0004(4)
C41	−0.0710(4)	0.2476(4)	0.3401(2)	0.0080(5)	0.0131(5)	0.00185(9)	0.0003(9)	−0.0003(4)	0.0007(4)
C42	−0.0870(4)	0.3871(4)	0.3226(2)	0.0084(5)	0.0115(5)	0.00266(11)	0.0025(8)	0.0001(4)	−0.0003(4)
C42′	−0.0595(5)	0.4349(4)	0.2548(2)	0.0158(7)	0.0105(5)	0.00364(13)	0.0065(9)	0.0017(5)	0.0038(4)
C43	−0.1402(5)	0.4808(5)	0.3679(2)	0.0129(6)	0.0155(6)	0.00341(13)	0.0071(10)	−0.0006(5)	−0.0034(5)
C44	−0.1847(5)	0.4450(6)	0.4290(2)	0.0107(6)	0.0260(8)	0.00325(13)	0.0127(11)	−0.0019(5)	−0.0068(6)
C44′	−0.2328(6)	0.5525(7)	0.4799(3)	0.0197(8)	0.0372(11)	0.00469(18)	0.0258(14)	−0.0032(7)	−0.0114(7)
C45	−0.1871(5)	0.3038(6)	0.4431(2)	0.0116(6)	0.0298(9)	0.00215(11)	0.0106(12)	0.0016(4)	−0.0003(5)
C46	−0.1351(4)	0.2019(5)	0.4000(2)	0.0095(6)	0.0204(7)	0.00207(10)	0.0043(10)	0.0006(4)	0.0025(4)
C46′	−0.1550(6)	0.0467(6)	0.4190(2)	0.0194(8)	0.0271(8)	0.00275(11)	0.0090(14)	0.0052(5)	0.0083(5)

H6	0.0447(0)	−0.1534(0)	0.3932(0)	5.0000(0)
H7	0.2202(0)	0.1038(0)	0.4332(0)	5.0000(0)
H8	0.4746(0)	0.1552(0)	0.3694(0)	5.0000(0)
H9	0.4576(0)	−0.0718(0)	0.2887(0)	5.0000(0)
H10	0.1878(0)	−0.2620(0)	0.3035(0)	5.0000(0)
H12	−0.2484(0)	−0.2235(0)	0.1678(0)	5.0000(0)
H13	−0.2992(0)	−0.4467(0)	0.1003(0)	5.0000(0)
H14	−0.0813(0)	−0.5347(0)	0.0618(0)	5.0000(0)
H15	0.1882(0)	−0.4009(9)	0.0945(0)	5.0000(0)
H16	0.2417(0)	−0.1785(0)	0.1622(0)	5.0000(0)
H22	−0.0430(0)	0.1422(0)	0.0475(0)	5.0000(0)
H22′	−0.0647(0)	0.0358(0)	0.1026(0)	5.0000(0)
H22″	−0.0231(0)	0.2068(0)	0.1214(0)	5.0000(0)
H23	0.1963(0)	0.1785(0)	−0.0033(0)	5.0000(0)
H24	0.4351(0)	0.2237(0)	−0.0644(0)	5.0000(0)
H24′	0.5923(0)	0.3151(0)	−0.0220(0)	5.0000(0)
H24″	0.5668(0)	0.1458(0)	−0.0416(0)	5.0000(0)
H25	0.6279(0)	0.1922(0)	0.0885(0)	5.0000(0)
H26	0.4832(0)	0.1342(0)	0.2459(0)	5.0000(0)
H26′	0.6087(0)	0.0828(0)	0.2017(0)	5.0000(0)
H26″	0.6225(0)	0.2515(0)	0.2178(0)	5.0000(0)
H32	0.3070(0)	0.4029(0)	0.1798(0)	5.0000(0)
H33	0.5094(0)	0.6277(0)	0.2048(0)	5.0000(0)
H34	0.5938(0)	0.7221(0)	0.3127(0)	5.0000(0)
H35	0.4732(0)	0.5948(0)	0.3982(0)	5.0000(0)
H36	0.2589(0)	0.4135(0)	0.3769(0)	5.0000(0)
H42	−0.0233(0)	0.3618(0)	0.2282(0)	5.0000(0)
H42′	−0.1599(0)	0.4456(0)	0.2354(0)	5.0000(0)
H42″	0.0221(0)	0.5275(0)	0.2579)0)	5.0000(0)
H43	−0.1461(0)	0.5752(0)	0.3557(0)	5.0000(0)
H44	−0.2246(0)	0.6445(0)	0.4626(0)	5.0000(0)
H44′	−0.3433(0)	0.5114(0)	0.4908(0)	5.0000(0)
H44″	−0.1610(0)	0.5680(0)	0.5188(0)	5.0000(0)
H45	−0.2259(0)	0.2737(0)	0.4842(0)	5.0000(0)
H46	−0.1152(0)	−0.0106(0)	0.3856(0)	5.0000(0)
H46′	−0.0940(0)	0.0513(0)	0.4598(0)	5.0000(0)
H46″	−0.2685(0)	0.0014(0)	0.4236(0)	5.0000(0)

The form of the anisotropic thermal parameter is: exp[−(B1,1) × H × H + B(2,2) × K × K + B(3,3) × L × L + B(1,2) × H × K + B(1,3) × H × L + B(2,3) × K × L)].

TABLE II. Interatomic Distances (A) and Angles (°).

Bond	Dist	Bond	Dist
Co–C(1)	2.046(3)	Co–C(6)	2.052(3)
Co–C(2)	2.039(3)	Co–C(7)	2.044(3)
Co–C(3)	2.014(3)	Co–C(8)	2.074(3)
Co–C(4)	2.116(3)	Co–C(9)	2.090(4)
Co–C(5)	2.285(3)	Co–C(10)	2.068(3)
C(1)–C(2)	1.436(4)	C(6)–C(7)	1.402(5)
C(2)–C(3)	1.438(4)	C(7)–C(8)	1.394(5)
C(3)–C(4)	1.445(4)	C(8)–C(9)	1.405(6)
C(4)–C(5)	1.468(4)	C(9)–C(10)	1.421(5)
C(5)–C(1)	1.473(4)	C(10)–C(6)	1.385(5)
C(5)–O	1.242(3)		
C(1)–C(11)	1.475(4)	C(2)–C(21)	1.508(4)
C(3)–C(31)	1.483(4)	C(4)–C(41)	1.489(4)
Phenyl Ring 1 [C(11) to C(16)] Ave.			1.381(4)
Phenyl Ring 2 [C(21) to C(26) Ave.			1.387(8)
Phenyl Ring 3 [C(31) to C(36)] Ave.			1.380(6)
Phenyl Ring 4 [C(41) to C(46)] Ave.			1.389(10)
C(22)–C(22)′	1.512(5)	C(42)–C(42)′	1.498(5)
C(24)–C(24)′	1.510(5)	C(44)–C(44)′	1.513(6)
C(26)–C(26)′	1.491(5)	C(46)–C(46)′	1.505(6)
Bond Angles			
C(1)–C(2)–C(3)	107.6(3)	C(6)–C(7)–C(8)	108.7(4)
C(2)–C(3)–C(4)	108.5(3)	C(7)–C(8)–C(9)	107.8(3)
C(3)–C(4)–C(5)	108.2(3)	C(8)–C(9)–C(10)	107.3(4)
C(4)–C(5)–C(1)	105.1(3)	C(9)–C(10)–C(6)	108.3(4)
C(5)–C(1)–C(2)	108.6(3)	C(10)–C(6)–C(7)	107.9(3)
C(1)–C(2)–C(21)	124.4(3)	C(1)–C(5)–O	127.9(3)
C(2)–C(3)–C(31)	124.5(3)	C(2)–C(1)–C(11)	125.3(3)
C(3)–C(4)–C(41)	125.3(3)	C(3)–C(2)–C(21)	125.5(3)
C(4)–C(5)–O	126.8(3)	C(4)–C(3)–C(31)	127.0(3)
C(5)–C(1)–C(11)	125.1(3)	C(5)–C(4)–C(41)	124.4(3)
Phenyl Ring 1 [C(11) to C(16)] Ave.			120.0(6)
Phenyl Ring 2 [C(21) to C(26)] Ave.			120.0(9)
Phenyl Ring 3 [C(31) to C(36)] Ave.			120.0(5)
Phenyl Ring 4 [C(41) to C(46)] Ave.			119.9(11)
C(1)–C(11)–C(12)	120.4(3)	C(2)–C(21)–C(22)	114.6(3)
C(1)–C(11)–C(16)	122.3(3)	C(2)–C(21)–C(26)	126.2(3)
C(12)–C(11)–C(16)	117.3(3)	C(22)–C(21)–C(26)	118.8(3)
C(3)–C(31)–C(32)	120.9(3)	C(4)–C(41)–C(42)	118.8(3)
C(3)–C(31)–C(36)	120.5(3)	C(4)–C(41)–C(46)	123.9(3)
C(32)–C(31)–C(32)	118.6(3)	C(42)–C(41)–C(46)	117.2(3)
C(22)′–C(22)–C(21)	122.5(3)	C(42)′–C(42)–C(41)	123.0(3)
C(22)′–C(22)–C(23)	117.5(4)	C(42)′–C(42)–C(43)	117.1(3)
C(24)′–C(24)–C(23)	122.6(4)	C(44)′–C(44)–C(43)	122.8(5)
C(24)′–C(24)–C(25)	121.3(5)	C(44)′–C(44)–C(45)	120.2(2)
C(26)′–C(26)–C(25)	118.4(4)	C(46)′–C(46)–C(45)	118.1(3)
C(26)′–C(26)–C(21)	121.4(4)	C(46)′–C(46)–C(41)	123.1(3)

(continued on facing page)

TABLE II. *(continued)*

Torsion Angles	
C(1)–C(2)–C(21)–C(22)	63.5
C(1)–C(2)–C(21)–C(26)	−123.6
C(2)–C(3)–C(31)–C(32)	42.2
C(2)–C(3)–C(31)–C(36)	−137.9
C(3)–C(4)–C(41)–C(42)	46.8
C(3)–C(4)–C(41)–C(46)	−136.3
C(5)–C(1)–C(11)–C(12)	23.0
C(5)–C(1)–C(11)–C(16)	−156.6

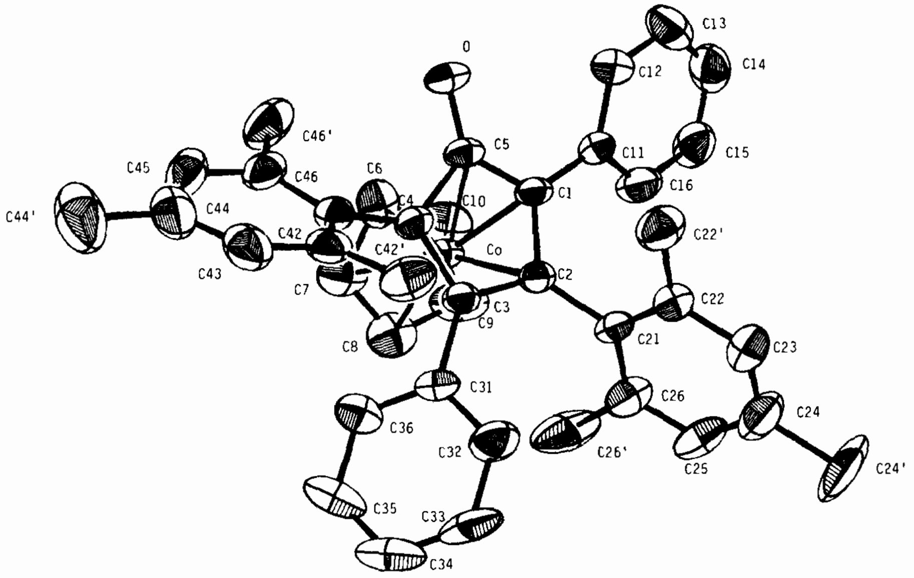


Fig. 1. A perspective view of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}(C_9H_{11})_2(C_6H_5)_2C_5O)$ showing the labeling system used in the text and Tables. Hydrogens have been omitted for clarity but bear the same numbers as the carbons to which they are bonded. Thermal ellipsoids are at the 50% probability level [11].

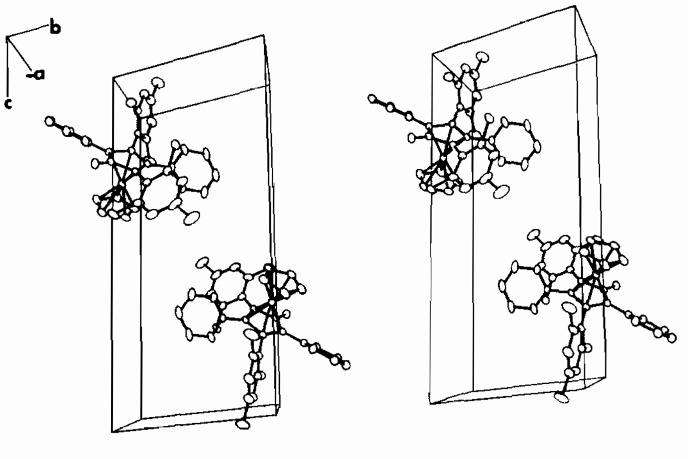


Fig. 2. A stereoscopic view of the unit cell contents.

used as a check of possible crystal decay. Orientation control reflections were checked every 400 data points. A small decay in the standards (~8%) during data collection was later corrected by an interpolation program [3].

A total of 5341 reflections were scanned out to $2\theta = 50°$. Of these 3385 had intensities $I \geqslant 3\sigma(I)$ and were considered to be observed. Here, $\sigma(I) = [S^2(C + R^2B) + (PI)^2]^{1/2}$ and $I = S(C - RB)$; where S = scan rate, C = total integrated peak count, R = ratio of background to the total counting time, B = background counts, P = 0.07. The data were corrected for Lorentz and polarization effects but not for absorption due to the low value of $\mu(6.078\ cm^{-1})$. In the structure solution and refinement the space group was assumed to be $P\bar{1}$ and this was vindicated by the completeness of refinement.

Solution and Refinement of Structure

The single cobalt atom was placed from the trivial Patterson solution and immediately gave a residual, R_F, of 0.42 where $R_F = (\Sigma\|F_o|-|F_c\|)/\Sigma F_o$. Two subsequent difference Fourier maps placed all the remaining non-hydrogen atoms and isotropic full-matrix least squares refinement [3] reduced R_F to 0.137. The thermal parameters were then refined with anisotropic motion leading to $R_F = 0.062$. Positional parameters for the 37 hydrogen atoms in the structure were then calculated based upon their expected ideal geometry and C–H = 0.95 Å. These were included as a fixed contribution to the least squares refinement giving a final R_F of 0.044 and a weighted residual, $R_w(F) = [\Sigma W(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, of 0.055. Refinement was considered complete when the shifts in the parameters were less than ~1.0 their estimated standard deviations. The function minimized in the refinement was $\Sigma w(|F_o|-|F_c|)^2$ with the weights, w, assigned by the expression $w = 1/\sigma(F_o)^2$ and $\sigma(F_o)^2 = [\sigma(I)^2 + (pI^2)^2]^{1/2}/LP$. The final e.s.d. of an observation of unit weight was 1.47. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber [4], corrected for (both real and imaginary parts) anomalous dispersion. Scattering factors for hydrogen were taken from Stewart, *et al.* [5].

The final difference Fourier was featureless with a number of peaks of height < ±0.2 $eÅ^{-3}$ distributed in a random fashion throughout the map. A Table of structure factors is available [6].

TABLE III. Mean Planes and Atomic Displacements Therefrom (in A).

A. Cyclopentadienyl Ring C(6), C(7), C(8), C(9), C(10			
$-0.5636x + 0.4656y - 0.6856z = -6.7187$			$\chi^2 = 1$
C(6)	−0.003(4)	C(9)	0.001(5)
C(7)	0.003(4)	C(10)	0.003(4)
C(8)	0.000(5)	Co	1.687(1)
B. Keto ring C(1), C(2), C(3), C(4), C(5)			
$-0.5714x + 0.4531y - 0.6840z = -3.3371$			$\chi^2 = 1503$
C(1)	−0.079(3)	C(4)	−0.047(3)
C(2)	0.052(4)	C(5)	0.077(3)
C(3)	−0.002(4)	Co	−1.691(1)
C. Phenyl Ring 1 C(11), C(12), C(13), C(14), C(15), C(16)			
$-0.0857x + 0.5848y - 0.08067z = -3.9795$			$\chi^2 = 11$
C(11)	0.007(1)	C(14)	0.008(1)
C(12)	−0.002(1)	C(15)	−0.002(1)
C(13)	−0.005(1)	C(16)	−0.005(1)
Co	−1.280(1)	C(1)	0.022(3)
D. Phenyl Ring 2 C(21), C(22), C(23), C(24), C(25), C(26)			
$0.1293x - 0.95561y - 0.2628z = -1.3403$			$\chi^2 = 110$
C(21)	0.026(3)	C(22)′	−0.130(4)
C(22)	−0.009(4)	C(24)′	+0.011(7)
C(23)	−0.011(1)	C(26)′	−0.148(6)
C(24)	0.015(5)	C(2)	−0.043(3)
C(25)	0.002(5)	Co	0.291(0)
C(26)	−0.024(4)		
E. Phenyl Ring 3 C(31), C(32), C(33), C(34), C(35), C(36)			
$0.8801x - 0.4710y - 0.0139z = -0.2498$			$\chi^2 = 42$
C(31)	0.014(4)	C(34)	0.011(4)
C(32)	−0.014(4)	C(35)	−0.012(5)
C(33)	0.002(6)	C(36)	−0.001(4)
Co	1.398(1)	C(3)	0.061(3)
F. Phenyl Ring 4 C(41), C(42), C(43), C(44), C(45), C(46)			
$-0.8501x - 0.3359y - 0.4050 = -1.9755$			$\chi^2 = 589$
C(41)	−0.062(4)	C(4)	−0.193(3)
C(42)	0.035(4)	C(42)	0.251(4)
C(43)	0.017(4)	C(44)′	−0.150(6)
C(44)	−0.044(4)	C(46)′	0.201(5)
C(45)	0.015(4)		
C(46)	0.036(4)		

Description of the Structure

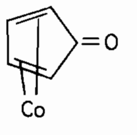
Table I gives the positional and anisotropic thermal parameters for the non-hydrogen atoms and the calculated parameters for the hydrogen atoms. A perspective view of the molecule, showing the thermal motion and numbering scheme used in the Tables, is presented in Fig. 1. Relevant bond distances and angles are given in Table II.

The structure consists of two five membered rings π-bonded to cobalt in the familiar sandwich manner. The cyclopentadienyl ring is bonded in a pentahapto-mode with all the carbons being essentially equidistant from the cobalt atom. These bond distances range from 2.044(3) to 2.090(4) Å with the average being 2.066(8) Å [7]. The cobalt ring-centroid distance is 1.687(1) Å. The ring is strictly planar as shown from the mean plane calculation in Table III.

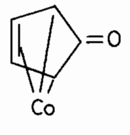
The cyclopentadienone ring is not planar nor are all the atoms equidistant from the metal atom. Rather, the keto carbonyl carbon atom is significantly farther removed from the cobalt atom than the other ring carbons. C(4) is also at a somewhat longer distance from the cobalt atom and this may be due to steric repulsions arising from the interactions of the mesityl group protons with hydrogens on the cyclopentadienyl ring. Considering other portions of the ring, it is found that the plane formed by C1, C4, C5, O is reasonably planar with $\chi^2 = 68$. However, the atoms in the fragment C1, C2, C3, C4 deviate significantly ($\chi^2 = 177$) from the mean plane formed by them. The dihedral angle formed by the intersection of these planes is 10.9°. This angle is considerably less than similar angles observed for tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron(0) [8] (20.1°), η^5-cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt(I) [9] (21.3°) but similar to the angles observed for 3,4-bis-(1-propynyl)-2,5-dimethylcyclopentadienone)tricarbonyliron(0) [2] (14.1°) and η^5-cyclopentadienyltetramethylcyclopentadienonecobalt(I) (9°) [10]. The phenyl and mesityl substituents are mildly electron donating groups and therefore one might expect a dihedral angle of this magnitude [2].

A better description of the cyclopentadienone ring results by considering mean planes through O, C(5), C(1), C(11), ($\chi^2 = 2$), and C(2), C(3), C(31), C(4) ($\chi^2 = 4$). Deviations of these atoms from their respective mean planes is ±0.003(3). However, these fragments are twisted about each other such that C(5) is farther away from the cobalt atom while C(1) and C(11) are tilted towards it. Similarly, C(2) is up while C(4) lies down towards the cobalt. These two planes intersect with a dihedral angle of 8.8°.

The carbon–carbon bond lengths C(1)–C(2), C(2)–C(3), C(3)–C(4) are identical within 2 e.s.d. while the other bond lengths within the cyclopentadienone ring are somewhat longer. This strongly implies essentially equal contributions from structures I and II.



I



II

Similar bond lengths are observed in other metal-cyclopentadienones [2, 8, 9].

The two five membered rings lie almost parallel to each other as the dihedral angle between their mean planes is 0.6°. C(1) in the keto ring lies oppsite C(10) in the cyclopentadienyl ring at a distance of 3.29 Å. This is shorter than the Ring 1–(Cp)–Ring 2(keto) distance of 3.38 Å. Furthermore, the C(1)–C(7) and C(1)–C(8) distances are equal to each other (4.05 Å) as are the C(1)–C(6) and C(1)–C(9) distances (4.58 Å). Thus, the rings are in the eclipse conformation.

The substituent phenyl groups are bonded to carbons 1 and 3 while the mesityl groups are bonded to C2 and C4. Torsional angles, given in Table II, show that the rings are twisted about the cyclopentadienone ring so as to minimize steric interactions. In spite of this there are two short hydrogen–hydrogen interactions, H(6)–H(46)′, 2.13 Å, and H(9)–H(26), 2.15 Å. These interactions are similar to those observed in (η^5-cyclopentadienyl)-(η^4-1,3-dimesityl-2,4-diphenylcyclobutadiene)cobalt and by analogy are sufficient to create a sizeable barrier to rotation about the two mesitylcyclopentadienone bonds as was indicated previously by ^{1}H NMR studies [1]. There are also numerous intramolecular close hydrogen–hydrogen contacts.

It should be noted that the mesityl rings are far from planar as was also the case for mesityl groups in (η^5-cyclopentadienyl)-(η^4-1,3-dimesityl-2,4-di-phenylcyclobutadiene) cobalt. The distortions are mainly due to the carbon atoms having short contacts with the cyclopentadienone ring. If these atoms are omitted, then the remaining atoms in each ring form fairly regular planes (C(22), C(23), C(24), C(25), C(26), $\chi^2 = 15$, and C(42), C(43), C(44), C(45), C(46), $\chi^2 = 59$).

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