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STUDIES ON THE REACTIONS OF (η^5-CYCLOPENTADIENYL)DICARBONYLCOBALT WITH PHENYL-1-NAPHTHYLACETYLENE AND WITH PHENYL-2-NAPHTHYLACETYLENE, AND AN X-RAY CRYSTALLOGRAPHIC DETERMINATION OF ONE OF THE PRODUCTS: (η^5-CYCLOPENTADIENYL)-[η^4-1,3-DI-(1-NAPHTHYL)-2,4-DIPHENYLCYCLOBUTADIENE]COBALT

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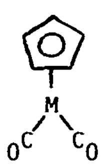
SUMMARY

The reactions of (η^5-C_5H_5)Co(CO)$_2$ with both phenyl-1-naphthylacetylene and phenyl-2-naphthylacetylene have been shown to produce all four possible η^4-cyclobutadiene-cobalt complexes and all six possible η^4-cyclopentadienone-cobalt derivatives. The structures of the η^4-cyclobutadiene-cobalt complexes have been assigned on the basis of proton NMR and mass spectral studies, and unequivocally established by means of an X-ray diffraction investigation for one of the isomers as (η^5-cyclopentadienyl)[η^4-1,3-di(1-naphthyl)-2,4-diphenylcyclobutadiene]cobalt. This compound is triclinic, $a = 10.88(2)$,

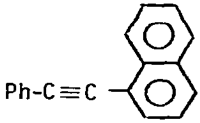
$b = 15.710(6)$, $c = 8.728(4)$ Å, $\alpha = 95.09(4)°$, $\beta = 101.94(2)°$, $\gamma = 86.93(3)°$. The space group is $P\bar{1}$ with $Z = 2$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares methods (4128 reflections above 3σ) to a final $R = 0.036$. Bond distances and angles are normal but the cyclobutadiene ring is not quite planar. One of the atoms is 0.047 Å out of the plane of the other three apparently to relieve steric stress. The two phenyl rings are almost coplanar with the cyclobutadiene ring (torsion angles 3.9 and 20.4°) while the naphthyl rings are almost perpendicular to it (torsion angles 63.8, 64°).

INTRODUCTION

The formation, reactions and structures of η^4-cyclobutadiene-metal complexes continues to be a highly active area of organic and organometallic chemistry [1]. Our own joint studies in this area have been concerned with the synthesis, mechanism of formation, and structural elucidation of products resulting from reactions of either $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (1) or $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ (2) with various symmetrical or unsymmetrical acetylenes. It was of interest to include in our program studies on reactions of (1) with both phenyl-1-naphthylacetylene (3) and phenyl-2-naphthylacetylene (4), since four structurally isomeric η^4-cyclobutadiene-cobalt derivatives might be anticipated from such interactions, and since an analysis of the spectral and structural properties of the products could lead to important comparisons with our earlier findings on phenyl [2,9], ferrocenyl [8], 2-thienyl [6], trimethylsilyl [4,5] and phenanthro [7] analogs.



(1) M = Co
(2) M = Rh



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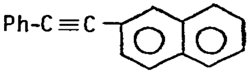


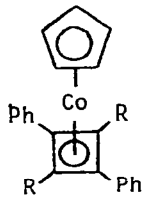
(4)

In this paper, reactions between (1) and both (3) and (4) are described in detail,* and the results of a single-crystal X-ray diffraction study of one of the resulting η^4-cyclobutadiene-cobalt complexes is discussed.

RESULTS AND DISCUSSION

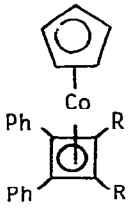
Synthesis and Spectral Considerations

As noted earlier, the interaction of (1) and an unsymmetrical acetylene such as (3) can in principle lead to two structurally isomeric (η^5-cyclopentadienyl)-[η^4-diphenyldi(1-naphthyl)cyclobutadiene]cobalt complexes and three structurally isomeric (η^5-cyclopentadienyl)-[η^4-diphenyldi(1-naphthyl)-cyclopentadienone)cobalt complexes. When (1) and (3) were allowed to react in refluxing toluene for 48 hours, both η^4-cyclobutadiene-cobalt complexes (5) and (6) as well as all three η^4-cyclopentadienone-cobalt complexes (7) were in fact observed to be formed, the former in 81% combined yield and the latter in 8% combined yield. The two complexes (5) and (6) were best separated by fractional crystallization techniques. The less soluble, higher-melting product was initially assigned as the more symmetrical 1,3-isomer (5) on the basis of its physical properties and comparisons with previous studies



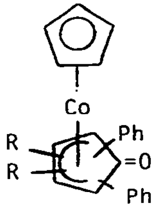
(5) R = 1-$C_{10}H_7$

(8) R = 2-$C_{10}H_7$



(6) R = 1-$C_{10}H_7$

(9) R = 2-$C_{10}H_7$



(7) R = 1-$C_{10}H_7$

(10) R = 2-$C_{10}H_7$

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*The reaction between (1) and (3) has been previously discussed in brief [3].

[4,5,8,9], and was confirmed as this isomer by means of X-ray analysis as is described below. The more soluble, lower-melting product was then assigned as the less symmetrical 1,2-isomer (6), although crystals suitable for X-ray analysis could not be obtained in this case. The proton NMR spectra of (5) and (6) exhibited singlet resonances for the η^5-C_5H_5 protons at δ 4.92 and 4.86 ppm, respectively, as well as multiplet resonances for the aromatic protons between δ 6.7-7.9 ppm for each complex.

As anticipated from earlier studies involving isomeric η^4-cyclobutadiene-cobalt complexes [4,5,8,9], mass spectral comparisons of (5) and (6) have proved valuable in making structural assignments. The mass spectrum of (5) showed, in addition to an intense molecular ion at m/e 580, strong fragmentation peaks resulting from the loss of acetylene (3) at m/e 352 as well as for (3) itself at m/e 228. Peaks due to the losses of either diphenylacetylene or di(1-naphthyl)acetylene from the molecular ion were observable but of low intensity, and peaks due to these symmetrical acetylenes were barely detectable in the mass spectrum of (5). In contrast, the mass spectrum of (6) exhibited the major peaks found for (5) at m/e 580, 352 and 228, as well as moderately intense bands at m/e 407 ($M - C_6H_5C_2C_6H_5^+$), 302 ($M - C_{10}H_7C_2C_{10}H_7^+$), 278 ($C_{10}H_7C_2C_{10}H_7^+$), and 178 ($C_6H_5C_2C_6H_5^+$). Assuming that extensive rearrangement of the tetraarylcyclobutadiene moiety does not occur before fragmentation of the acetylenic units, the mass spectral results for both (5) and (6) are thus consistent with the proposed structures.

The three η^5-cyclopentadienone-cobalt complexes (7) were isolated via column chromatography and also by extraction of the filtered insolubles from the reaction mixture. The three isomers could be separated by means of preparative TLC techniques. Elemental analyses for these complexes consistently indicated low values for carbon and cobalt, and high values for hydrogen and oxygen. However, calculations involving one mole of water per mole of complex produced values which in each case were in good agreement with the found elemental compositions. These complexes apparently tenaciously hold water due probably to the highly polar nature of the carbonyl group of the coordinated cyclopentadienone ring. The three isomers were further characterized as η^4-cyclopentadienone-cobalt complexes (7) by means of mass spectrometry (M^+, m/e 608) and by distinct η^5-cyclopentadienyl proton resonances in their proton NMR spectra. More definitive structural assignments for the individual isomers of (7) cannot be made on the basis of the data presently available, however.

In an analogous manner, a reaction between (1) and (4) in refluxing xylene for 48 hours afforded an 86% combined yield of the (η^5-cyclopentadienyl)-[η^4-diphenyldi(2-naphthyl)cyclobutadiene]cobalt complexes (8) and (9), as well as a mixture of (η^5-cyclopentadienyl)[η^4-diphenyldi(2-naphthyl)cyclopentadienone]cobalt isomers (10) in 1.6% combined yield. η^4-Cyclobutadiene-cobalt isomer (8) (M^+ = m/e 508, δCp = 4.66 ppm, m.p. 243-245°C) was best purified by fractional crystallization techniques, whereas η^4-cyclobutadiene-cobalt isomer (9) [M^+ = m/e 508, δCp = 4.64 ppm, m.p. 211-215°C(dec)]

Table I. Crystal Data

Crystal System: Triclinic

$a = 10.88(2)$ Å
$b = 15.710(6)$ Å
$c = 8.728(4)$ Å
$\alpha = 95.09(4)°$
$\beta = 101.94(2)°$
$\gamma = 86.93(3)°$

Volume	1453 $Å^3$	
d_{calcd}	1.33	g/cm^3
d_{obsd}	1.32(2)	g/cm^3
Molec. Wt.	580.6	
Z	2	
F(000)	604	
Space Group	$P\bar{1}$	
$\mu(\lambda=0.71069$ Å)	6.45 cm^{-1}	

was most conveniently purified by preparative TLC methods. Assignments of these two products as the 1,3-isomer (8) and the 1,2-isomer (9), respectively, has been made on the basis of their physical properties as well as on their mass spectral cracking patterns, as discussed above for isomers (5) and (6). These assignments must be considered as tentative, however, until X-ray diffraction studies on one or both of the products are undertaken.

In view of the very low yields of the η^4-cyclopentadienone-cobalt isomers (10) produced in this reaction, no detailed separation studies were undertaken, although TLC again indicated three isomers to be present. An analytically pure sample of one of the isomers was obtained, however, by fractional crystallization techniques, and was characterized by its proton NMR spectrum (δCp = 4.96 ppm), by its mass spectrum (M^+ m/e 608), and by elemental analysis. The latter indicated an unhydrated product in this instance.

Crystallographic Considerations - Crystal Structure of Compound (8)

Bond lengths and angles are summarized in Tables III and IV. Mean planes are given in Table V. Figure 1 is an ORTEP [10] drawing of the molecule with the numbering scheme used in the Tables.

The cyclopentadiene ring is planar. Bond distances within this ring range from 1.382(4) Å to 1.406(4) Å with an average bond length of 1.389(7) Å. Bond angles range from 107.6(2)° to 108.3(3)° [avg. 108.0(4)°].

The cyclobutadiene ring deviates slightly from planarity. If a plane is chosen through any three of the carbon atoms, the fourth atom lies 0.047 Å out of the plane. Similar deviations from planarity were noted earlier [9]. Bond lengths range from 1.462(2) Å to 1.470(2) Å and average 1.466(4) Å. Bond angles are close to 90°. The dihedral angle between the best planes defined by the carbon atoms of the four- and five-membered rings is 3.1°.

Cobalt-carbon distances appear normal. The Co-C(cb) distances range from 1.967(2) Å to 1.997(2) Å with an average of 1.980(14) Å. Co-C(cp) distances vary from 2.043(2) Å to 2.063(2) Å and average 2.054(9) Å. The

(continued on p. 118)

Table II. 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)
C01	0.21557(3)	0,18206(2)	0.13471(3)	0.00634(2)	0.00327(1)	0.00995(4)	-0.00094(3)	0.00161(5)	0.00256(3)
C1	0.1822(2)	0,1873(1)	-0.0964(2)	0.0051(2)	0.00335(9	0.0098(3)	-0.0013(2)	0.0019(4)	0.0015(3)
C2	0.0720(2)	0.2138(1)	-0.0300(2)	0.0054(2)	0.00339(9	0.0090(3)	-0.0014(2)	0.0028(3)	0.0019(3)
C3	0.1367(2)	0.2902(1)	0.0493(2)	0.0055(2)	0.00314(8	0.0091(3)	-0.0011(2)	0.0025(4)	0.0022(3)
C4	0.2485(2)	0.2623(1)	-0.0127(2)	0.0055(2)	0.00308(8	0.0091(3)	-0.0009(2)	0.0026(4)	0.0014(3)
C5	0.1943(3)	0.1513(2)	0.3501(3)	0.0148(3)	0.00932(18	0.0154(4)	0.0052(4)	0.0113(6)	0.0141(4)
C6	0.3138(3)	0.1838(2)	0.3627(3)	0.0131(3)	0.00577(14	0.0121(4)	0.0014(4)	-0.0040(6)	0.0029(4)
C7	0.3770(3)	0.1307(2)	0.2677(4)	0.0091(3)	0.00532(13	0.0197(5)	0.0024(3)	-0.0015(6)	0.0076(4)
C8	0.2990(3)	0.0656(2)	0.1956(4)	0.0175(4)	0.00364(11	0.0203(5)	0.0019(4)	-0.0017(8)	0.0053(4)
C9	0.1855(3)	0.0777(2)	0.2451(4)	0.0142(3)	0.00710(13	0.0274(5)	-0.0076(3)	-0.0070(7)	0.0192(4)
C10	0.2128(2)	0.1168(1)	-0.2032(2)	0.0064(2)	0.00327(9	0.0096(3)	-0.0002(2)	0.0024(4)	0.0017(3)
C11	0.3318(2)	0.1082(2)	-0.2388(3)	0.0071(2)	0.00460(12	0.0174(4)	-0.0002(3)	0.0056(5)	-0.0009(4)
C12	0.3635(3)	0.0410(2)	-0.3362(4)	0.0102(2)	0.00536(13	0.0211(5)	0.0036(3)	0.0129(5)	0.0013(4)
C13	0.2765(3)	-0.0197(2)	-0.4024(3)	0.0171(4)	0.00405(12	0.0144(4)	0.0040(3)	0.0099(6)	0.0002(4)
C14	0.1581(3)	-0.0111(2)	-0.3701(3)	0.0141(3)	0.00377(11	0.0154(4)	-0.0030(3)	0.0025(6)	-0.0018(4)
C15	0.1257(2)	0.0561(2)	-0.2725(3)	0.0086(2)	0.00384(10	0.0147(4)	-0.0022(3)	0.0047(5)	-0.0002(3)
C16	-0.0625(2)	0.1932(1)	-0.0628(3)	0.0053(2)	0.00325(9	0.0138(3)	-0.0014(2)	0.0037(4)	-0.0001(3)
C17	-0.1152(2)	0.1615(2)	0.0496(3)	0.0072(2)	0.00533(12	0.0180(4)	-0.0032(3)	0.0079(5)	0.0019(4)
C18	-0.2453(3)	0.1510(2)	0.0265(4)	0.0079(2)	0.00702(16	0.0258(5)	-0.0048(3)	0.0123(5)	0.0005(5)
C19	-0.3201(2)	0.1724(2)	-0.1075(4)	0.0058(2)	0.00645(15	0.0316(6)	-0.0036(3)	0.0086(6)	-0.0013(5)
C20	-0.2729(2)	0.2032(2)	-0.2302(4)	0.0066(2)	0.00401(11	0.0224(5)	-0.0002(3)	-0.0031(6)	-0.0038(4)
C21	-0.1405(2)	0.2132(1)	-0.2086(3)	0.0061(2)	0.00279(9	0.0159(4)	-0.0005(2)	0.0008(5)	-0.0012(3)
C22	-0.0929(3)	0.2439(2)	-0.3308(3)	0.0088(2)	0.00429(11	0.0155(4)	-0.0010(3)	-0.0033(5)	0.0023(4)
C23	-0.1714(3)	0.2650(2)	-0.4676(4)	0.0156(4)	0.00561(14	0.0183(5)	-0.0019(4)	-0.0053(7)	0.0053(4)
C24	-0.3030(3)	0.2559(2)	-0.4841(4)	0.0129(3)	0.00686(17	0.0234(6)	0.0009(4)	-0.0180(7)	0.0035(5)

Table II. 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)
C25	-0,3498(3)	0.2268(2)	-0,3692(4)	0,0085(3)	0.00643(17	0,0291(7)	0,0004(4)	-0,0001(8)	-0,0006(6)
C26	0,0965(2)	0.3686(1)	0.1301(2)	0,0068(2)	0.00329(9	0,0097(3)	-0,0002(2)	0,0032(4)	0,0013(3)
C27	-0,0131(2)	0.3739(2)	0.1886(3)	0.0098(2)	0.00440(12	0.0221(4)	-0,0027(3)	0,0140(5)	-0,0029(4)
C28	-0,0510(3)	0.4491(2)	0.2615(4)	0.0114(3)	0.00600(15	0.0268(5)	-0,0002(3)	0,0195(6)	-0,0049(5)
C29	0,0198(3)	0.5203(2)	0,2795(4)	0.0131(3)	0.00423(12	0.0230(5)	0,0011(3)	0,0129(6)	-0,0036(4)
C30	0,1277(3)	0.5164(2)	0.2221(4)	0,0132(3)	0.00356(11	0,0253(5)	-0,0025(3)	0,0137(6)	-0,0027(4)
C31	0,1662(2)	0.4415(2)	0.1481(3)	0.0097(2)	0.00380(11	0,0203(4)	-0,0018(3)	0,0127(5)	-0,0008(4)
C32	0,3638(2)	0.3065(1)	-0,0197(3)	0.0054(2)	0.00297(8	0,0129(3)	-0,0015(2)	0,0050(4)	0.0002(3)
C33	0,4614(2)	0.3153(2)	0.1076(3)	0.0074(2)	0,00511(12	0,0161(4)	-0,0039(3)	0,0007(5)	0,0036(4)
C34	0,5684(3)	0.3610(2)	0.1028(4)	0.0082(2)	0.00673(14	0.0241(6)	-0,0070(3)	-0,0036(6)	0,0050(5)
C35	0,5767(3)	0.3965(2)	-0,0297(4)	0.0086(2)	0.00684(14	0.0299(6)	-0,0083(3)	0,0052(6)	0,0059(5)
C36	0,4796(2)	0.3911(2)	-0.1622(3)	0.0092(2)	0.00444(11	0.0217(4)	-0,0035(3)	0,0111(5)	0.0038(4)
C37	0,3701(2)	0.3456(1)	-0.1582(3)	0.0067(2)	0.00308(9	0.0139(3)	-0,0009(2)	0,0080(4)	0,0006(3)
C38	0,2705(2)	0.3437(2)	-0.2918(3)	0.0090(2)	0.00437(11	0.0140(3)	-0,0017(3)	0,0067(5)	0.0031(3)
C39	0,2773(3)	0.3849(2)	-0.4216(3)	0,0140(3)	0,00593(14	0.0147(4)	-0,0016(4)	0,0074(6)	0.0052(4)
C40	0,3853(3)	0.4287(2)	-0.4248(4)	0.0176(4)	0.00770(16	0.0220(4)	-0,0053(4)	0,0149(6)	0.0118(4)
C41	0,4831(3)	0.4307(2)	-0.3012(4)	0.0143(3)	0.00732(15	0,0279(5)	-0.0065(3)	0.0172(6)	0.0099(5)
H5	0,1298(0)	0.1775(0)	0.4057(0)	6.0390(0)					
H6	0,3445(0)	0.2363(0)	0.4219(0)	5.2930(0)					
H7	0,4647(0)	0.1365(0)	0.2523(0)	5.0400(0)					
H8	0.3214(0)	0.0166(0)	0.1192(0)	5.5290(0)					
H9	0,1121(0)	0.0380(0)	0.2096(0)	6.2590(0)					
H11	0.3944(0)	0.1530(0)	-0.1893(0)	4.2840(0)					

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H12           0.4507(0)   0.0334(0)  -0.3605(0)    5.1730(0)
H13           0.3050(0)  -0.0700(0)  -0.4751(0)    5.1380(0)
H14           0.0975(0)  -0.0556(0)  -0.4186(0)    5.0170(0)
H15           0.0387(0)   0.0633(0)  -0.2468(0)    3.9360(0)
H17          -0.0594(0)   0.1458(0)   0.1603(0)    4.4650(0)
H18          -0.2918(0)   0.1301(0)   0.1125(0)    5.5030(0)
H19          -0.4127(0)   0.1662(0)  -0.1220(0)    5.6910(0)
H22           0.0005(0)   0.2485(0)  -0.3164(0)    4.4020(0)
H23          -0.1347(0)   0.2867(0)  -0.5563(0)    6.2110(0)
H24          -0.3594(0)   0.2714(0)  -0.5813(0)    6.4820(0)
H25          -0.4443(0)   0.2226(0)  -0.3811(0)    6.3430(0)
H27          -0.0630(0)   0.3205(0)   0.1759(0)    4.8320(0)
H28          -0.1305(0)   0.4541(0)   0.3056(0)    5.7610(0)
H29          -0.0097(0)   0.5765(0)   0.3352(0)    5.3260(0)
H30           0.1780(0)   0.5702(0)   0.2353(0)    5.3260(0)
H31           0.2452(0)   0.4407(0)   0.1037(0)    4.4520(0)
H33           0.4553(0)   0.2888(0)   0.2064(0)    4.3170(0)
H34           0.6396(0)   0.3674(0)   0.1994(0)    5.8240(0)
H35           0.6528(0)   0.4302(0)  -0.0323(0)    5.9440(0)
H38           0.1938(0)   0.3115(0)  -0.2884(0)    4.0990(0)
H39           0.2021(0)   0.3815(0)  -0.5166(0)    5.5680(0)
H40           0.3927(0)   0.4566(0)  -0.5220(0)    6.5200(0)
H41           0.5608(0)   0.4619(0)  -0.3048(0)    6.5130(0)

-----------------------------------------------------------

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:
EXP[-(B(1,1)*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 III.

Interatomic Distances (Å)

Atoms	Distance	Atoms	Distance
Co1-C1	1.983(2)	C10-C11	1.390(3)
Co1-C2	1.967(2)	C10-C15	1.390(3)
Co1-C3	1.997(2)	C11-C12	1.372(3)
Co1-C4	1.975(2)	C12-C13	1.384(4)
Co1-C5	2.043(2)	C13-C14	1.372(4)
Co1-C6	2.053(2)	C14-C15	1.376(3)
Co1-C7	2.063(2)	C16-C17	1.375(3)
Co1-C8	2.062(2)	C16-C21	1.427(3)
Co1-C9	2.048(2)	C17-C18	1.405(3)
C1-C2	1.463(2)	C18-C19	1.338(4)
C1-C4	1.470(2)	C19-C20	1.411(4)
C1-C10	1.454(3)	C20-C21	1.430(3)
C2-C3	1.469(2)	C20-C25	1.391(4)
C2-C16	1.480(2)	C21-C22	1.408(3)
C3-C4	1.462(2)	C22-C23	1.372(3)
C3-C26	1.458(3)	C23-C24	1.422(4)
C4-C32	1.482(2)	C24-C25	1.339(4)
C5-C6	1.403(4)	C26-C27	1.387(3)
C5-C9	1.406(4)	C26-C31	1.387(3)
C6-C7	1.382(4)	C27-C28	1.377(3)
C7-C8	1.387(4)	C28-C29	1.372(4)
C8-C9	1.389(4)	C29-C30	1.366(3)
		C30-C31	1.379(3)
		C32-C33	1.372(3)
		C32-C37	1.419(3)
		C33-C34	1.410(3)
		C34-C35	1.348(4)
		C35-C36	1.396(4)
		C36-C37	1.431(3)
		C36-C41	1.419(4)
		C37-C38	1.418(3)
		C38-C39	1.370(3)
		C39-C40	1.400(4)
		C40-C41	1.349(4)

cobalt to ring centroid distances are 1.687 Å and 1.672 Å for the four- and five-membered rings respectively.

The dimensions of the cyclobutadiene and cyclopentadiene rings and the cobalt to carbon distances are in good agreement with those found in similar compounds [11,12].

Bond distances and bond angles within the phenyl rings appear normal. The C-C bond distances range from 1.339(3) Å to 1.431(3) Å. The C-C-C bond angles range from 117.8(2)° to 123.0(2)°. The average value of the bond distance between the cyclobutadiene ring and a naphthyl group [1.481(1) Å] is somewhat longer than the corresponding average value for the phenyl groups [1.456(2) Å]. Bond angles associated with two cyclobutadiene carbon atoms and the first carbon of a phenyl ring have a mean value of 134.3°. One phenyl ring is almost coplanar with the cyclobutadiene ring as seen by the C4-C1-C10-C11 torsion angle (Table IV) of 3.9°.

(continued on p. 122)

Table IV.

Bond Angles (°)

Atoms	Angle	Atoms	Angle
C2-C1-C4	90.1(1)	C2-C16-C17	121.0(2)
C2-C1-C10	135.0(2)	C2-C16-C21	119.1(2)
C4-C1-C10	134.9(2)	C17-C16-C21	119.6(2)
C2-C1-C3	89.9(1)	C16-C17-C18	121.5(2)
C1-C2-C16	136.7(2)	C17-C18-C19	119.6(2)
C3-C2-C16	130.9(2)	C18-C19-C20	122.4(2)
C2-C3-C4	90.2(1)	C19-C20-C21	118.5(2)
C2-C3-C26	134.0(2)	C19-C20-C25	123.0(2)
C4-C3-C26	134.9(2)	C21-C20-C25	118.5(3)
C1-C4-C3	89.8(1)	C16-C21-C20	118.4(2)
C1-C4-C32	136.0(2)	C16-C21-C22	122.8(2)
C3-C4-C32	132.2(2)	C20-C21-C22	118.7(2)
C6-C5-C9	107.6(2)	C21-C22-C23	121.1(2)
C5-C6-C7	107.8(2)	C22-C23-C24	118.8(3)
C6-C7-C8	108.7(2)	C23-C24-C25	120.9(2)
C7-C8-C9	108.3(3)	C20-C25-C24	122.0(3)
C5-C9-C8	107.6(2)	C3-C26-C27	121.7(2)
C1-C10-C11	120.4(2)	C3-C26-C31	120.6(2)
C1-C10-C15	121.8(2)	C27-C26-C31	117.7(2)
C11-C10-C15	117.8(2)	C26-C27-C28	120.9(2)
C10-C11-C12	121.3(2)	C27-C28-C29	120.6(2)
C11-C12-C13	120.2(2)	C28-C29-C30	119.3(2)
C12-C13-C14	119.0(2)	C29-C30-C31	120.5(2)
C13-C14-C15	121.0(2)	C26-C31-C30	121.0(2)
C10-C15-C14	120.6(2)	C4-C32-C33	121.7(2)
		C4-C32-C37	119.1(2)
		C33-C32-C37	119.0(2)
		C32-C33-C34	121.5(2)
		C33-C34-C35	119.9(2)
		C34-C35-C36	121.4(2)
		C35-C36-C37	119.2(2)
		C35-C36-C41	122.8(2)
		C37-C36-C41	118.0(2)
		C32-C37-C36	119.0(2)
		C32-C37-C38	122.7(2)
		C36-C37-C38	118.3(2)
		C37-C38-C39	121.4(2)
		C38-C39-C40	119.8(2)
		C39-C40-C41	120.6(2)
		C36-C41-C40	121.8(2)

Torsion Angles	
C4-C1-C10-C11	3.9
C1-C2-C16-C21	-63.8
C2-C3-C26-C27	20.4
C1-C4-C32-C37	64.0

Table V.

Deviations of Atoms (Å) from Least-Squares Planes

The equation of the plane is of the form

$$A*X + B*Y + C*Z - D = 0$$

a) Plane through C1, C2, C3, C4

$$-.0643X + 0.5800Y - 0.7979Z + 2.0062 = 0$$

C1	0.012
C2	-0.012
C3	0.012
C4	-0.012

b) Plane through C5, C6, C7, C8, C9

$$-.0634X + 0.6211Y - 0.7643Z + 1.2268 = 0$$

C5	- .002
C6	0.001
C7	0.000
C8	-0.001
C9	0.002

c) Plane through C10, C11, C12, C13, C14, C15

$$-.1157X + 0.6077Y - 0.7857Z - 2.2442 = 0$$

C10	- .009
C11	0.005
C12	0.002
C13	-0.006
C14	0.002
C15	0.005

d) Plane through C16, C17, C18, C19, C20, C21, C22, C23, C24, C25

$$0.1406X - 0.9069Y - 0.3973Z + 2.6025 = 0$$

C16	-0.013	C21	0.007
C17	-0.003	C22	0.016
C18	0.016	C23	0.011
C19	0.003	C24	-0.012
C20	0.012	C25	-0.019

Table V. Con't.

e) Plane through C26, C27, C28, C29, C30, C31

$$-0.3264X + 0.3489Y - 0.875Z - 0.6493 = 0$$

C26	-0.002
C27	-0.002
C28	0.005
C29	-0.005
C30	0.001
C31	0.002

f) Plane through C32, C33, C34, C35, C36, C37, C38, C39, C40, C41

$$0.4593X - 0.8121Y - 0.3600Z + 1.9265 = 0$$

C32	0.022	C37	0.033
C33	-0.024	C38	0.005
C34	-0.038	C39	-0.036
C35	0.008	C40	-0.026
C36	0.031	C41	0.025

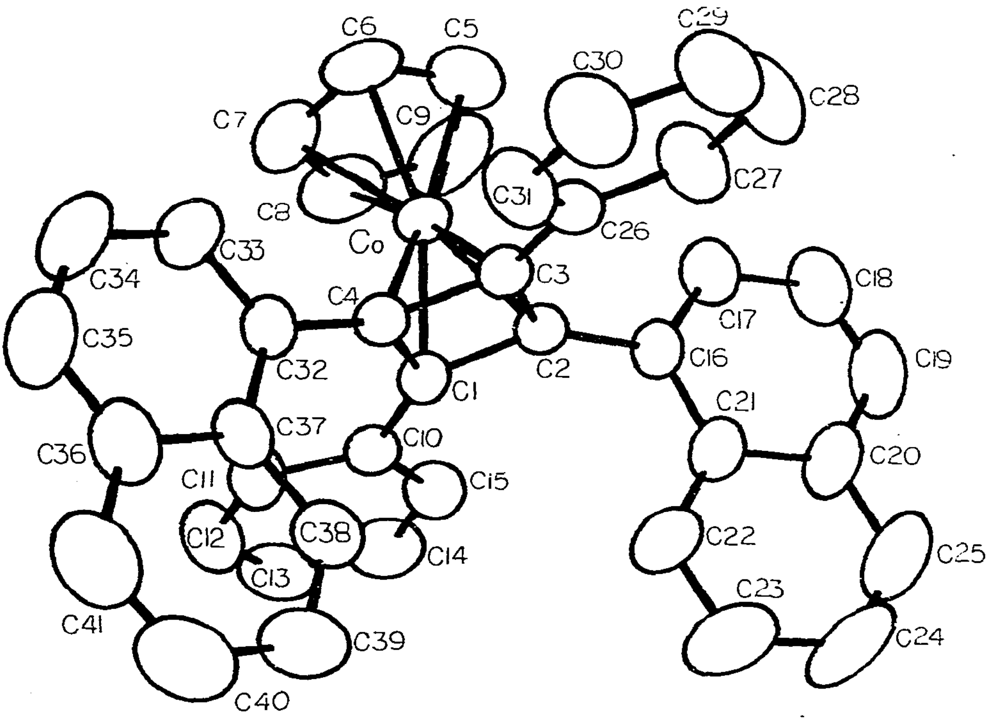

Fig. 1. A perspective view of Compound (6) with the numbering scheme used in the tables.

The other phenyl ring is twisted somewhat more out of this plane (20.4°) while the naphthyl rings sterically avoid phenyl rings by twisting almost perpendicular to the cyclobutadiene plane.

The shortest intra- and intermolecular contacts between hydrogen atoms are listed in Table VI. The shortest contact distance between two non-hydrogen atoms is C9 . . . C13 [8] = 3.49 Å. A packing diagram of the unit cell is shown in Fig. 2.

Table VI.

Nonbonded Hydrogen Contacts (Å)

H5···H17[1]	2.68	H11···H19[4]	2.08
H6···H25[2]	2.58	H24···H33[5]	2.46
H6···H33[1]	2.65	H24···H34[5]	2.54
H7···H33[1]	2.46	H29···H38[6]	2.59
H9···H15[3]	2.44	H40···H41[7]	2.22
H9···H17[1]	2.46		

Symmetry Operations

[1]	x, y, z
[2]	1+x, y, 1+z
[3]	$\bar{x}, \bar{y}, \bar{z}$
[4]	1+x, y, z
[5]	x-1, y, z-1
[6]	x, 1+y, z
[7]	1-x, 1-y, 1+z
[8]	x, y, 1+z

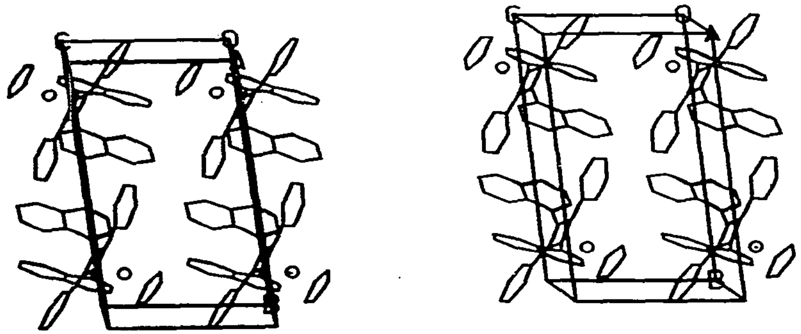

Fig. 2. A stereoview of the packing in a unit cell of Compound (6).

EXPERIMENTAL SECTION

All melting points were taken in sealed capillaries under nitrogen and are uncorrected. CAMAG neutral grade alumina was used for column chromatography. Columns were wrapped in aluminum foil to minimize photodecomposition. Pyridine was dried over KOH and distilled from BaO, xylene was dried over CaH_2 and distilled. 1-Iodonaphthalene and 2-iodonaphthalene were purchased from Eastman Organic Chemicals Company and from K and K Laboratories, respectively. $(h^5\text{-}C_5H_5)Co(CO)_2$ [2] and cuprous phenylacetylide [17] were prepared by literature procedures. ^1H NMR spectra were recorded on a Varian A-60 instrument, ^{13}C NMR spectra on a Varian CFT-20 instrument, IR spectra on a Beckman IR-10 instrument, and mass spectra on a Perkin-Elmer-Hitachi RMV-6L instrument at 70 eV. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of Phenyl-1-naphthylacetylene

In a 500-ml, 3-necked flask equipped with a condenser, nitrogen inlet and mercury overpressure valve were added 300 ml of pyridine, 15.28 g (60 mmol) of 1-iodonaphthalene, and 10 g (60 mmol) of cuprous phenylacetylide. The system was flushed repeatedly with nitrogen and heated to reflux with magnetic stirring for 24 hours. The dark solution was allowed to cool to room temperature under nitrogen and then diluted with 600 ml of water. Following several ether extractions and clarification with activated charcoal, the concentrated extracts were washed several times with one liter volumes each of 5% hydrochloric acid, 5% sodium bicarbonate, and water. After drying over $MgSO_4$, the solution was filtered and the ether was evaporated. A brown oil which remained was solidified by immersion of the beaker into a bath of dry ice-methanol. This method yielded 11.5 g (84%) of crude product, m.p. 48-50°C. Further purification was accomplished by recrystallization from an ethanol-water mixture to produce 9.22 (67%) of phenyl-1-naphthylacetylene, m.p. 52-53° (Found: C, 94.77; H, 5.44. $C_{18}H_{12}$ calcd: C, 94.70; H, 5.30. The ^1H NMR spectrum ($CDCl_3$)

exhibited an aromatic proton resonance between τ 2.0-3.0 ppm, whereas the IR spectrum (KBr) contained a $\gamma_{C\equiv C}$ absorption of 2190 cm^{-1}.

Preparation of Phenyl-2-naphthylacetylene

Phenyl-2-naphthylacetylene was prepared in a manner analogous to that described above starting with 2-iodonaphthalene, cuprous phenylacetylide and pyridine. The product was obtained in 67% yield, m.p. 113-114°C (lit. [18] m.p. 117°C).

Reaction of η^5-Cyclopentadienyldicarbonyl Cobalt and Phenyl-1-naphthylacetylene

A mixture of 6.85 g (30 mmol) of phenyl-1-naphthylacetylene, 2.70 g (15 mmol) of $(h^2\text{-}C_5H_5)Co(CO)_2$ and 250 ml of xylene was added to a 500-ml, 3-necked flask equipped with a condenser, nitrogen inlet, magnetic stirrer and mercury overpressure valve. The system was flushed with nitrogen several times and the flask was covered with aluminum foil to exclude light. The reaction mixture was heated to reflux for 48 hours, after which time TLC indicated that all the acetylene had been consumed. After cooling, the reaction mixture was filtered in air, and the filtrate concentrated and placed on a 1" x 20" column of alumina which had been packed in benzene.

A broad red-brown band was eluted with benzene and produced 7.0 g (81%) of a mixture of (η^5-cyclopentadienyl)-[η^4-1,3-di-(1-naphthyl)-2,4-diphenylcyclobutadiene]cobalt (5) and (η^5-cyclopentadienyl)-[η^4-1,2-di-(1-naphthyl)-3,4-diphenylcyclobutadiene]cobalt (6). The isomers were separated by fractional crystallization from a benzene/heptane solvent mixture. A pure sample of (5) was obtained from initial crops in the form of deep red crystals, m.p. 279-280°C (Found: C, 84.75; H, 4.97; Co, 10.15. $C_{41}H_{29}Co$ calcd: C, 84,81; H, 5.03; Co, 10.15%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at 84.92(s) and δ 6.7-7.9 (m) ppm assignable to the $h^5\text{-}C_5H_5$ and aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3175-3000(m), 1590(m), 1500(m), 1450(m), 1020(m), 1000(m), 800-690(s) cm^{-1}. The mass spectrum exhibited the following principal peaks: m/e 580 (77, M^+), 402 (2, $M-C_6H_5C_2C_6H_5^+$) 352 (50, $M-C_6H_5C_2C_{10}H_2^+$), 302 (9, $M-C_{10}H_7C_2C_{10}H_7^+$), 278 (1, $C_{10}H_7C_1C_{10}H_7^+$), 228 (55, $C_6H_5C_2C_{10}H_7^+$), 178 (1, $C_6H_5C_2C_6H_5^+$), 124 (100, $C_5H_5Co^+$), 59 (14, Co^+).

As successive crops were taken, they became increasingly concentrated with isomer (6). This technique led eventually to a pure sample of (6) in the form of fine yellow crystals, m.p. 241-242°C (Found: C, 84.84; H, 5.11; Co, 10.08%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at δ 4.86(s) and δ 6.7-7.9(m) ppm assignable to the h^5-C_5H_5 and aromatic protons, respectively. The IR spectrum contained major bands at 3100-3000(w), 1590(m), 1500(m), 1475(m), 1445(w), 1020(w), 1000(w), 800-690 cm^{-1}. The mass spectrum exhibited the following principal peaks: m/e 580 (100, M^+), 402 (17, $M-C_6H_5C_2C_6H_5^+$), 352 (45, $M-C_6H_5C_2C_{10}H_7^+$), 302 (27, $M-C_{10}H_7C_2C_{10}H_7^+$), 278 (20, $C_{10}H_7C_2C_{10}H_7^+$), 228 (55, $C_6H_5C_2C_{10}H_7^+$), 178 (5, $C_6H_5C_2C_6H_5^+$), 129 (100, $C_5H_5Co^+$), 59 (28, Co^+)

Continued elution with benzene removed a second band which yielded 50 mg of an unidentified compound. A ^1H NMR spectrum of the product exhibited absorptions characteristic of aromatic protons; however, h^5- C_5H_5 absorptions were absent.

A third band (red) was eluted with 1:1 benzene-chloroform. Evaporation of the solvent left 260 mg. of the (η^5-cyclopentadienyl)-[η^4-di-(1-naphthyl)-diphenylcyclopentadienone]cobalt isomers (7). At this point, the original residue which had been separated by filtration of the reaction mixture was extracted and the extracts concentrated to give an additional 460 mg of (7) (Total yield = 720 mg, 8%). TLC indicated that three products were present. Separation of these compounds was accomplished by coating 50 mg portions of the mixture on preparative TLC plates and multiply eluting with chloroform. The three complexes (7) had R_f values in $CHCl_3$ of 0.23, 0.14 and 0.06, respectively.

The isomer of highest R_f was removed from the plates, extracted with chloroform, and next from benzene/heptane. After drying in vacuo at 100°, 195 mg. of product was obtained, m.p. 380°C(dec.) (Found: C, 80.24; H, 5.22; Co, 9.22; O, 5.43. $C_{42}H_{29}CoO$ calcd; C, 82,88; H, 4.80; Co, 9.68; O, 2.63%. $C_{42}H_{29}CoO_2$ calcd.: C, 80.51; H, 4.95; Co, 9.42; O, 5.11 %). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at δ 5.38(s) and 6.67-8.34(m) ppm assignable to the h^5-C_5H_5 and the aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3175-3000(w), 1590(s), 1500(w), 1450(m), 1028(w), and 900-700(w) cm^{-1}. The mass spectrum contained an intense peak at m/e 608 (M^+).

A second isomer of (7) of second highest R_f was removed from the plates extracted with chloroform, and next from benzene/heptane. After drying in vacuum at 100°, 100 mg. of product was obtained, m.p. 330°C(dec) (Found: C, 80.45; H, 5.19; Co, 9.24; O, 4.82%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at δ 5.15(s) and 6.67-8.34(m) ppm assignable to the h^5-C_5H_5 and the aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3175-3000(m), 1590(s), 1500(m0, 1450(m), 1028(w), 900-700(s) cm^{-1}. The mass spectrum contained an intense peak at m/e 608 (M^+).

A third isomer of (7) of lowest R_f was removed from the plates, extracted with chloroform, and next from benzene/heptane. After drying in vacuo at 100°; 12.5 mg of product was obtained, m.p. 321°(dec) (Found: C, 80.28; H, 5.35; Co, 8.38; O, 5.98%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at δ 5.23(s) and 6.67-8.34(m) assignable to the h^5-C_5H_5 and the aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3020-2900(m), 1590(s), 1500(w), 1450(w), 1260(s), 1200-975(s), 800(s), and 700(m) cm^{-1}. The mass spectrum contained an intense band at m/e 608 (M^+).

From a typical preparative TLC plate, the isomers of (7) were isolated in the following relative amounts: 19.5 mg/10.0 mg/1.2 mg (16:8:1), respectively.

Reaction of h^5-Cyclopentadienyldicarbonyl cobalt and Phenyl-2-naphthylacetylene

Xylene (250 ml), phenyl-2-naphthylacetylene (6.85 g, 30 mmol) and (h^5-C_5H_5)Co(CO)$_2$ (2.70 g, 15 mmol) were added to a 500-ml, 3-necked flask equipped as above. The flask was covered with aluminum foil, the contents were degassed several times under nitrogen, and the mixture heated to reflux for 48 hours. At the end of this period, TLC indicated that all the acetylene had been consumed. After cooling, the reaction mixture was filtered in air, the filtrate was concentrated, and placed on a 1" x 20" column of alumina which had been packed in benzene.

The first band (red-brown) was eluted with benzene and yielded 7.45 g (86%) of a mixture of (η^5-cyclopentadienyl)-[h^5-1,3-di(2-naphthyl)-2,4-diphenylcyclobutadiene]cobalt (8) and (η^5-cyclopentadienyl)-[h^4-1,2-di(2-naphthyl)-3,4-diphenylcyclobutadiene]cobalt (9). Separation of these isomers could be accomplished either by preparative TLC [using benzene/heptane (1:4) as the eluent], or by fractional crystallization [using benzene/heptane (1:1)]. A pure sample of (8) (highest R_f) was obtained by several fractional crystallizations of the first crop of crystals from band one. This technique yielded (8) in the form of fine yellow crystals which, after drying in vacuo at 100°, had a m.p. of 243-245°C. (Found: C, 84.53; H, 5.08, Co, 10.01%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks at δ 4.65(s) and 7.15-7.88(m) ppm, assignable to the h^5-C_5H_5 and the aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3150-3000(w), 1650-1600(s), 1500(m), 1000(m), and 860-690(s) cm^{-1}. The mass spectrum exhibited the following principal peaks: m/e 580 (88, M^+), 402 (4, $M - C_6H_5C_2C_6H_5^+$), 352 (27, $M - C_6H_5C_2C_{10}H_7^+$), 302 (3, $M - C_{10}H_7C_2C_{10}H_7^+$), 278 (3, $C_{10}H_7C_2C_{10}H_7$), 228 (20, $C_6H_5C_2C_7H_{10}^+$), 178 (1, $C_6H_5C_2C_6H_5^+$), 124 (100, $C_5H_5Co^+$).

Isomer (9) was best separated by preparative TLC techniques. Several preparative TLC plates were coated with 50 mg portions of the isomeric mixture. Multiple elution with benzene/heptane (1:1) resulted in the development of two major bands. Removal of the band of lower R_f (yellow) followed by recrystallization from benzene/heptane afforded (9) as fine yellow crystals. After drying in vacuo at 100°C, (9) had a m.p. of 211-215°(dec) (Found: C, 85.09; H, 5.11; Co, 10.07%). The 'H NMR spectrum in $CDCl_3$ exhibited peaks at δ 4.64(s) and 7.15-7.88(m) ppm, assignable to the h^5- C_5H_5 and the aromatic protons, respectively. The IR spectrum (KBr) contained major bands at 3150-3000(m), 1650-1595(s), 1500(m), 1000(m), and 860-690(s) cm^{-1}. The mass spectrum exhibited the following principal peaks: m/e 580 (100, M^+), 402 (11, $M-C_6H_5C_2C_6H_5^+$), 352 (36, $M-C_6H_5C_2C_{10}H_7^+$), 302 (6, $M-C_{10}H_7C_2C_{10}H_7^+$), 278 (5, $C_{10}H_7C_2C_{10}H_7^+$), 228 (16, $C_6H_5C_2C_{10}H_7^+$), 178 (21, $C_6H_5C_2C_6H_5^+$), 124 (42, $C_5H_5Co^+$).

A second band (orange-red) was eluted from the column with chloroform Evaporation of the solvent left 150 mg (1.6%) of the (η^5-cyclopentadienyl)-[h^4-di-(2-naphthyl)-diphenylcyclopentadienone]cobalt isomers (10). TLC indicated that three products were present. An analytically pure sample of one of these isomers was obtained by fractional crystallization from benzene/heptane (1:1). After drying in vacuo at 100°C, the product was obtained as fine red brown crystals, m.p. over 280° with dec. (Found: C, 83.03; H, 4.96; Co, 9.72; O, 2.36. $C_{42}H_{29}Co$ calcd: C, 82.88; H, 4.80; Co, 9.68; O, 2.63%). The ^1H NMR spectrum in $CDCl_3$ exhibited peaks of δ 4.96(s) and 7.0-7.8 ppm, assignable to the h^5-C_5H_5 and the aromatic proton, respectively. The IR spectrum (KBr) contained major bands at 3150-3000(m), 1650-1550(s), 1030-990(w), 900-700(w) cm^{-1}. The mass spectrum contained an intense peak at m/e 608 (M^+).

Crystallographic Studies

A parallelepiped shaped crystal with approximate dimensions 0.38 x 0.34 x 0.42 mm was used for the entire study. Unit cell dimensions and an orientation matrix for data collection were determined by least-squares refinement of 25 reflections, well centered on an Enraf-Nonius CAD-4 diffractometer using MoK_α radiation ($\bar{\lambda}$ = 0.71069 Å) monochromatized by reflection from an oriented graphite monochromator. The density was determined by flotation in a cyclohexane-carbon tetrachloride mixture. Crystallographic data are given in Table I. The choice of $P\bar{1}$ as the space group was confirmed by the successful solution of the structure.

Data were collected using the θ-2θ scan mode ($2\theta_{max}$ = 50°). Reflections were scanned at a variable rate ranging from 2°/min. for the weakest reflections 20°/min. for the strongest. The scan range was 0.70°. Backgrounds at either end of the scan were collected for one-fourth of the scan time. The intensities of three standard reflections ($1\bar{5}\bar{1}$, $1\bar{2}\bar{3}$, and $2\bar{2}\bar{1}$)

were monitored after every 60 intensity measurements. The intensities of these standard reflections varied ±2% with no systematic trends. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied since the linear absorption coefficient ($\mu = 6.45\ \mathrm{cm}^{-1}$) was small. Of the 5069 independent reflections which were measured, 4128 were found to have intensities greater than or equal to 3σ where $\sigma = [\text{total counts} + \text{background counts} + (pI)^2]^{\frac{1}{2}}$ and $p = 0.05$.

Solution and Refinement

A trial position for the cobalt atom was obtained from a three-dimensional Patterson summation. Successive difference electron density syntheses established the locations of the carbon atoms. Hydrogen atoms were placed in their calculated positions (C-H = 1.00 Å) and were not refined. Each hydrogen atom was assigned the isotropic temperature factor of the carbon atom to which it is bonded.

Least-squares refinement employed full-matrix methods. The function minimized was $\Sigma w(F_o - F_c)^2$, where $w = 1/\sigma_F^2$. Initially, isotropic temperature factors were used, but in the final refinements, all nonhydrogen atoms were refined assuming anisotropic thermal motion. The refinement converged with $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o| = 0.036$ and $R_2 = [(\Sigma w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{\frac{1}{2}} = 0.052$. For the final least-squares refinements, data were weighted by the function $w = 1/\sigma^2$ where $\sigma = [\sigma(I)^2 + (0.05I^2)^2]^{\frac{1}{2}}/LP$. A correction for anomalous dispersion was made for the cobalt atom ($\Delta f' = 0.299$, $\Delta f'' = 0.973$) [13]. The atomic scattering factors used for nonhydrogen atoms were the values of Cromer and Waber [14] and scattering factors for hydrogen were obtained from the calculation of Stewart, Davidson and Simpson [15].

In the last cycle of refinement, all shifts were less that one standard deviation with virtually all of the nonhydrogen atom parameters having a shift to error ratio of less than 0.50. The error in an observation of unit weight, Σ, was 1.58.

In the final difference synthesis, no peak greater than 0.28 e/Å was found. Peaks were distributed randomly throughout the map. Positional and thermal parameters for all the atoms are given in Table II. A Table of structure factors is available as supplementary material.* All programs used in the crystal structure study were part of the Enraf-Nonius structure determining package [16]

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* See NAPS document No. 03420 for 17 pages of supplementary material. Order from NAPS C/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $5.00 for photocopies or £3.00 for microfiche. Outside the U.S. and Canada add postage of $3.00 for photocopy and $1.00 for microfiche.

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