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STUDIES ON THE REACTIONS OF FERROCENYLPHENYLACETYLENE AND DIFERROCENYLACETYLENE WITH (η^5-CYCLOPENTADIENYL)DICARBONYLCOBALT, AND AN X-RAY CRYSTALLOGRAPHIC DETERMINATION OF ONE OF THE PRODUCTS: (η^5-CYCLOPENTADIENYL)(η^4-1,3-DIFERROCENYL-2,4-DIPHENYLCYCLOBUTADIENE)COBALT

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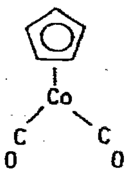
SUMMARY

The reaction of (η^5-C_5H_5)Co(CO)$_2$ and diferrocenylacetylene has been shown to produce the mixed sandwich complex (η^5-cyclopentadienyl)(η^4-tetraferrocenylcyclobutadiene)cobalt in 83% yield. A similar reaction between (η^5-C_5H_5)Co(CO)$_2$ and ferrocenylphenylacetylene produces two structural isomers, (η^5-cyclopentadienyl)(η^4-1,2-diferrocenyl-3,4-diphenylcyclobutadiene)cobalt and (η^5-cyclopentadienyl)(η^4-1,3-diferrocenyl-2,4-diphenylcyclobutadiene)cobalt, in 78% combined yield. The structures of these two products have been inferred from proton NMR and mass spectral studies, and unequivocally established by means of a single crystal X-ray diffraction investigation of the latter isomer.

(η^5-cyclopentadienyl)(η^4-1,3-diferrocenyl-2,4-diphenylcyclobutadiene) cobalt, $C_{41}H_{33}CoFe_2$, is monoclinic, $P2_1/c$ with a = 10.551(3), b = 16.345(2), c = 19.796(3) Å and β = 93.19°. However, the unit cell was found to contain 2 hexane molecules in addition to 4 parent molecules to yield a calculated density of 1.441 g/cm^{-3}. The measured density was 1.44(2) g/cm^{-3}. Intensity data were gathered by the θ-2θ scan method with an automated 4-circle diffractometer (CAD-4) yielding 7315 reflections (10,450 scanned) greater than 3σ. Refinement by full matrix least squares led to a final R of 0.039. The cyclobutadiene ring is square with average bond length of 1.462(5) Å. However, the ring is not quite planar, one of the carbons being 0.035 Å out of the plane formed by the other three. Other features of the structure are regular with the ferrocene C_5 rings being in the eclipsed conformation.

INTRODUCTION

Recent joint studies in our laboratories have been concerned with the synthesis, mechanism of formation, and structural elucidation of products resulting from reactions of (η^5-cyclopentadienyl)dicarbonylcobalt (1) with various unsymmetrical acetylenes.[1-6] It was of interest in this regard



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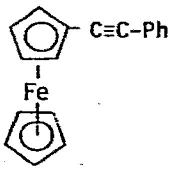

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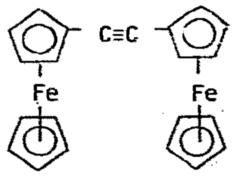

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to investigate the interactions of (1) with ferrocenylphenylacetylene (2) and with diferrocenylacetylene (3), since novel mixed metal sandwich complexes might be expected to result, and since both of these organometallic acetylenes are readily available as starting materials.[7]

Previous studies on the interactions of ferrocenylacetylenes (2) and (3) with metal carbonyls have been limited to reactions with $Co_2(CO)_8$, in which (2) is effectively cyclotrimerized and (3) is converted into tetraferrocenylcyclopentadienone, and to reactions of (3) with $Mo(CO)_6$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$, in which both tetraferrocenylcyclopentadienone and a variety of organo-iron complexes are produced.[8-10] In none of these investigations, however, were ferrocenyl-cyclobutadiene complexes detected, as might possibly be anticipated[11-13] from related reactions of diphenylacetylenes with these metal carbonyls.

We now describe reactions of (1) with the ferrocenylacetylenes (2) and (3) which lead to a variety of η^4-cyclobutadiene-cobalt complexes bearing ferrocenyl substituents, and report results of an X-ray crystallographic analysis of one of the products, (η^5-cyclopentadienyl)-(η^4-1,3-diferrocenyl-2,4-diphenylcyclobutadiene)cobalt (5), which unequivocally confirms the existence of the ferrocenylcyclobutadiene ring system in these substances.

RESULTS AND DISCUSSION

Synthesis and Spectral Considerations*

It was of initial interest to study the reactivity of diferrocenylacetylene (3) and η^5-cyclopentadienyldicarbonylcobalt (1), since (3) may be regarded as a metallo-aromatic acetylene, and might be expected to afford products similar to those found in the reaction of diphenylacetylene and (1).[1] When (3) and (1) were allowed to react in refluxing xylene, the cyclobutadiene complex (η^5-cyclopentadienyl)(η^4-tetraferrocenylcyclobutadiene)cobalt (4) was obtained in remarkably high yields (80-85%). These results

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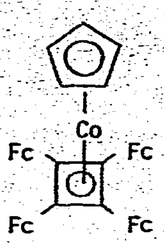
*Synthetic and spectral aspects of this program have previously been discussed in brief.[2]



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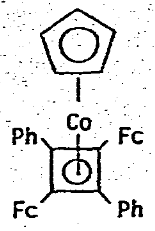

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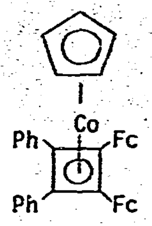

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thus indicate that steric factors which may be operative in earlier attempted cyclotrimerization reactions of (3) with metal carbonyls are not of significant importance in the cyclodimerization of (3) to form (4), a process which may involve cobaltacyclic intermediates.[2,14]

The high stability of (4), which may be regarded as a "super-sandwich" complex composed of four ferrocenyl and one η^5-cyclopentadienyl-η^4-cyclobutadienecobalt units, is indicated by the intense molecular ion in the mass spectrum of (4). The intensity of this peak dwarfs all others, although low intensity peaks representing losses of C_5H_5Co, $(C_5H_5)_2Fe$, acetylene (3), the cyclobutadiene moiety $C_4(C_{10}H_9Fe)_4$, etc., are also clearly evident and serve to confirm the structure of (4). The proton NMR spectrum of (4) contains absorptions for C_5H_5Co, C_5H_5Fe and C_5H_4Fe hydrogens whose multiplicities, relative intensities and chemical shift values are likewise in accord with the proposed structure. The aromatic reactivity of (4) and comparisons with related systems are currently under investigation.

As noted earlier, the interaction of an unsymmetrical acetylene such as (2) with (1) can theoretically produce two structurally isomeric cyclobutadiene complexes, such as the 1,3-diferrocenyl isomer (5) and the 1,2-diferrocenyl isomer (6).* As in previous studies involving unsymmetrical

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*These type products are more appropriately referred to as structural isomers rather than geometrical isomers. Earlier references to such products as "trans" and "cis" isomers therefore represents incorrect usage and terminology.

acetylenes,[3-6] both isomers (5) and (6) could in fact be obtained in a 78% combined yield from the reaction of (1) and (2) in refluxing xylene. Separation of (5) and (6) was achieved by fractional crystallization from hydrocarbon solvents, the more symmetrical isomer (5) being appreciably less soluble than (6).*

The proton NMR spectra of (5) and (6) are consistent with the proposed structures. The major differences in the two spectra occur in resonances representing the substituted cyclopentadienyl ring protons, which occur as a single A_2B_2 pattern for (5), and a less symmetrical pattern for (6), as have previously been noted.[15,16]

Further support for the structural assignments for isomers (5) and (6) arises from a consideration of their mass spectra. Intense molecular ions were observed in both cases, again attesting to the high stability of such cyclobutadiene complexes derived from ferrocenylacetylenes. As in the case of earlier studies on isomeric cyclobutadiene complexes arising from the reaction of (1) with phenyltrimethylsilylacetylene[5], however, mass spectral cracking patterns have proved valuable in structural assignments. Thus, the mass spectrum of (6) exhibited a major peak at m/e 410, representing loss of (2) from the molecular ion, as well as equally intense peaks at m/e 344 and 289 due to further fragmentation of the $(M - C_{10}H_9FeC_2C_6H_5{}^+)$ ion by additional losses of C_5H_6 and C_5H_5Fe units, respectively. In addition, peaks at m/e 518 and 302, corresponding to the losses of (3) and of diphenylacetylene from the molecular ion, were also clearly evident, as were ions representing the acetylenes themselves at m/e 394 and 178, respectively. Assuming that

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*Complexes (5) and (6) have independently been obtained by Yasafuku and Yamazaki from a reaction between (2) and $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$.[15,16] Structural assignments were inferred from proton NMR data, and are in agreement with our assignments based upon mass spectral and X-ray diffraction considerations.

a major fragmentation pathway of cyclobutadiene-metal complexes is one which proceeds via losses of acetylenes from the molecular ion, then all the ions observed above might be anticipated in the mass spectrum of (6).[2,4,17]

The mass spectral cracking pattern of (5) also exhibited major peaks at m/e 410, 344 and 289, representing losses of (2) and subsequent fragments from the molecular ion, as well as an intense peak representing the acetylene (2) at m/e 286. In contrast to the spectrum of (6), however, peaks due to losses of the symmetrical acetylenes (3) and diphenylacetylene as well as peaks due to the acetylenes themselves were totally absent. Assuming that rearrangement of the tetraarylcyclobutadiene moiety does not occur before fragmentation, the mass spectral results for (5) are therefore completely consistent with its assignment as the more symmetrical isomer.

Crystallographic Considerations

In order to unequivocally assign the structures of isomers (5) and (6), and to obtain meaningful molecular parameters relating to the assumed η^4-cyclobutadiene ring system, a single crystal X-ray diffraction investigation of the more crystallizable isomer (5) was subsequently undertaken.

Table I contains the positional and anisotropic thermal parameters for the non-hydrogen atoms. Isotropic temperature factors for the hydrogen atoms and solvent carbon atoms are given in Table II. A table of structure factors is available from the editor's office.* Figure 1 shows the numbering scheme used in the tables, while Figure 2 illustrates the molecular configuration and thermal motions[19] of the subject compound.

(Continued on p.254)

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*The table of structure factors has been deposited as NAPS Document No. 03225 (32 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $8.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States and Canada, postage is $3.00 for a photocopy and $1.00 for a fiche.

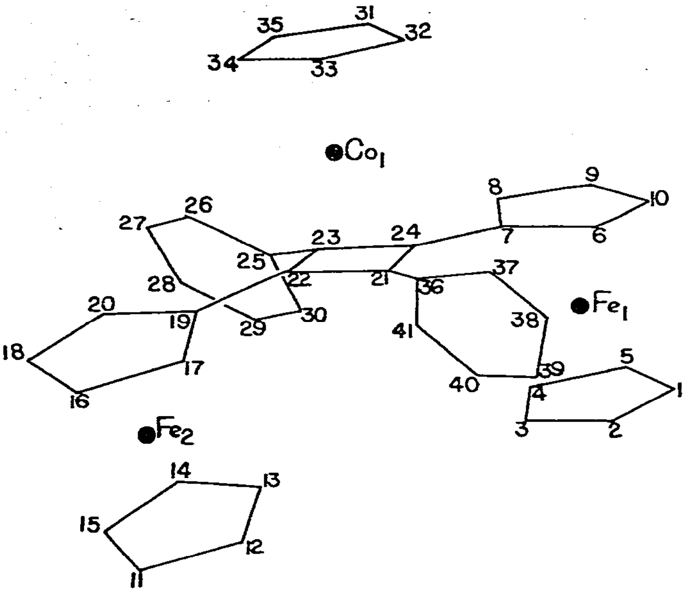

Fig. 1. Perspective view of compound 5 showing the numbering scheme used in the Tables.

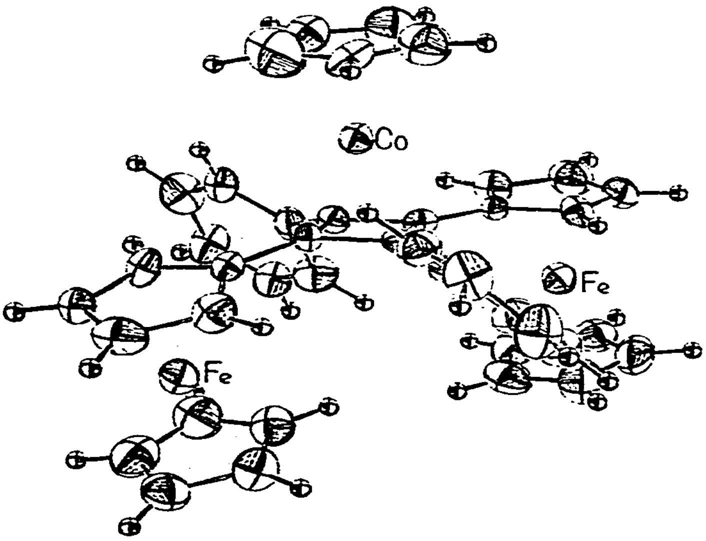

Fig. 2. ORTEP view of compound 5 with thermal ellipsoids at the 50% probability level.

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	0.64352(3)	0.17176(2)	0.19715(1)	0.00576(2)	0.00239(1)	0.00131(1)	-0.00098(2)	0.00036(2)	0.00046(1)
FE1	0.31605(3)	0.12301(2)	0.37031(2)	0.00569(2)	0.00261(1)	0.00165(1)	0.00037(3)	0.00135(2)	0.00000(1)
FE2	0.11419(3)	0.43046(2)	0.20958(2)	0.00620(2)	0.00262(1)	0.00172(1)	-0.00040(3)	0.00060(2)	-0.00009(2)
C1	0.1818(3)	0.0590(2)	0.4184(2)	0.0079(2)	0.00530(12	0.00311(7	-0.0008(3)	0.0027(2)	0.00313(15)
C2	0.2690(3)	0.0044(2)	0.3893(1)	0.0133(3)	0.00342(9	0.00287(7	-0.0027(3)	0.0015(3)	0.00236(14)
C3	0.3905(3)	0.0227(2)	0.4194(2)	0.0101(2)	0.00440(10	0.00336(8	0.0037(3)	0.0027(2)	0.00396(14)
C4	0.3787(3)	0.0867(2)	0.4649(1)	0.0117(3)	0.00591(14	0.00208(6	-0.0021(3)	-0.0007(2)	0.00261(16)
C5	0.2490(3)	0.1083(2)	0.4641(1)	0.0142(3)	0.00546(13	0.00217(6	0.0017(3)	0.0058(2)	0.00196(15)
C6	0.2998(2)	0.1445(1)	0.2678(1)	0.0058(2)	0.00300(7	0.00171(5	0.0003(2)	0.0001(1)	0.00115(11)
C7	0.4279(2)	0.1590(1)	0.2927(1)	0.0056(2)	0.00234(7	0.00145(4	-0.0002(2)	0.0007(1)	0.00062(9)
C8	0.4239(2)	0.2206(1)	0.3441(1)	0.0073(2)	0.00239(7	0.00214(5	-0.0001(2)	0.0016(2)	-0.00012(11)
C9	0.2953(2)	0.2438(1)	0.3501(1)	0.0092(2)	0.00235(8	0.00271(6	0.0019(2)	0.0031(2)	0.00029(12)
C10	0.2187(2)	0.1974(2)	0.3038(1)	0.0062(2)	0.00341(8	0.00258(6	0.0023(2)	0.0015(2)	0.00198(12)
C11	0.1026(3)	0.3197(2)	0.1615(2)	0.0116(3)	0.00322(10	0.00362(9	-0.0009(3)	0.0000(3)	-0.00209(16)
C12	0.2317(3)	0.3418(2)	0.1747(2)	0.0103(3)	0.00388(10	0.00317(8	0.0034(3)	0.0016(2)	-0.00099(16)
C13	0.2504(3)	0.4188(2)	0.1412(1)	0.0100(2)	0.00456(12	0.00272(7	-0.0002(3)	0.0040(2)	-0.00135(16)
C14	0.1317(3)	0.4415(2)	0.1079(1)	0.0132(3)	0.00436(11	0.00183(6	0.0018(3)	0.0013(2)	-0.00059(14)
C15	0.0408(3)	0.3807(2)	0.1215(1)	0.0107(3)	0.00465(11	0.00245(6	0.0007(3)	-0.0012(2)	-0.00262(14)
C16	0.0431(3)	0.4201(2)	0.3029(1)	0.0100(2)	0.00441(10	0.00214(6	-0.0046(3)	0.0019(2)	0.00124(13)
C17	0.1706(2)	0.4482(2)	0.3083(1)	0.0088(2)	0.00329(9	0.00165(5	-0.0014(2)	-0.0004(2)	0.00090(11)
C18	-0.0300(2)	0.4769(2)	0.2629(1)	0.0065(2)	0.00428(10	0.00257(6	-0.0018(2)	0.0029(2)	-0.00051(14)

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C19         0.1767(2)   0.5234(1)   0.2719(1)   0.0062(2)   0.00276( 7  0.00134( 4 -0.0004(2)   0.0008(1)   0.00012(10)
C20         0.0925(2)   0.5403(1)   0.2438(1)   0.0056(2)   0.00304( 8  0.00210( 5  0.0002(2)   0.0014(2)  -0.00029(11)
C21         0.5750(2)   0.0621(1)   0.2180(1)   0.0054(1)   0.00232( 7  0.00129( 4 -0.0009(2)   0.0004(1)   0.00011( 9)
C22         0.7090(2)   0.0699(1)   0.2397(1)   0.0057(2)   0.00236( 7  0.00133( 4 -0.0003(2)   0.0003(1)  -0.00018( 9)
C23         0.6773(2)   0.1311(1)   0.2903(1)   0.0054(1)   0.00236( 7  0.00126( 4 -0.0002(2)   0.0004(1)  -0.00007( 9)
C24         0.5425(2)   0.1219(1)   0.2699(1)   0.0056(2)   0.00219( 6  0.00133( 4 -0.0007(2)   0.0005(1)   0.00011( 9)
C25         0.7477(2)   0.1634(1)   0.3508(1)   0.0059(2)   0.00227( 7  0.00136( 4  0.0003(2)   0.0002(1)  -0.00025( 9)
C26         0.8578(2)   0.2098(1)   0.3475(1)   0.0068(2)   0.00297( 8  0.00152( 5 -0.0010(2)   0.0003(2)  -0.00004(10)
C27         0.9262(2)   0.2325(2)   0.4062(1)   0.0069(2)   0.00351( 9  0.00223( 6 -0.0022(2)  -0.0013(2)  -0.00022(13)
C28         0.8856(3)   0.2111(2)   0.4685(1)   0.0101(2)   0.00394(10  0.00176( 5 -0.0007(3)  -0.0018(2)  -0.00072(13)
C29         0.7756(3)   0.1660(2)   0.4726(1)   0.0108(3)   0.00456(11  0.00138( 5 -0.0012(3)   0.0006(2)  -0.00025(13)
C30         0.7073(2)   0.1427(2)   0.4141(1)   0.0076(2)   0.00382( 9  0.00155( 5 -0.0019(2)   0.0009(2)  -0.00027(12)
C31         0.5991(3)   0.2921(2)   0.1736(2)   0.0148(3)   0.00307(10  0.00414(10  0.0016(3)   0.0014(3)   0.00235(17)
C32         0.5402(3)   0.2417(2)   0.1236(2)   0.0122(3)   0.00687(15  0.00411( 9 -0.0034(4)  -0.0033(3)   0.00629(18)
C33         0.6511(4)   0.1983(2)   0.0968(1)   0.0325(6)   0.00453(12  0.00124( 6 -0.0097(4)   0.0013(3)   0.00090(14)
C34         0.7652(3)   0.2247(2)   0.1324(2)   0.0123(3)   0.00529(12  0.00315( 7 -0.0018(3)   0.0047(2)   0.00353(15)
C35         0.7206(3)   0.2825(2)   0.1784(1)   0.0141(3)   0.00350( 9  0.00269( 7 -0.0054(3)  -0.0007(3)   0.00209(14)
C36         0.5031(2)   0.0045(1)   0.1742(1)   0.0065(2)   0.00221( 7  0.00149( 4 -0.0005(2)   0.0000(1)   0.00007(10)
C37         0.3978(2)  -0.0359(1)   0.1971(1)   0.0082(2)   0.00273( 8  0.00226( 6 -0.0018(2)   0.0010(2)  -0.00046(12)
C38         0.3325(3)  -0.0934(2)   0.1572(2)   0.0090(2)   0.00319( 9  0.00330( 8 -0.0031(2)   0.0006(2)  -0.00058(15)
C39         0.3704(3)  -0.1118(2)   0.0940(1)   0.0097(2)   0.00313( 9  0.00272( 7 -0.0018(3)  -0.0024(2)  -0.00116(13)
C40         0.4768(3)  -0.0730(2)   0.0700(1)   0.0117(3)   0.00406(10  0.00158( 5 -0.0009(3)  -0.0011(2)  -0.00092(13)
C41         0.5416(2)  -0.0147(2)   0.1096(1)   0.0084(2)   0.00340( 9  0.00153( 5 -0.0017(2)   0.0004(2)  -0.00041(11)

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)].
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TABLE II

Positional and Thermal Parameters for Hydrogen Atoms and Solvent Molecule Carbon Atoms

Atom	X	Y	Z	β(ISO)
C42	0.2074(9)	0.1304(6)	0.0525(5)	16.5(3)
C43	0.1005(11)	0.0837(7)	0.0460(6)	19.3(3)
C44	0.0553(9)	0.0206(6)	0.0074(6)	17.8(3)
H1	0.092(3)	0.066(2)	0.403(2)	4.6(7)
H2	0.253(3)	-0.042(2)	0.350(1)	4.2(6)
H3	0.459(3)	0.002(2)	0.419(2)	7.4(9)
H4	0.427(4)	0.113(2)	0.479(2)	8.1(10)
H5	0.230(4)	0.155(2)	0.488(2)	8.3(11)
H6	0.267(2)	0.109(2)	0.231(1)	3.7(6)
H8	0.511(2)	0.237(2)	0.370(1)	3.8(6)
H9	0.273(2)	0.280(2)	0.374(1)	3.4(5)
H10	0.121(2)	0.203(2)	0.296(1)	3.1(5)
H11	0.069(3)	0.271(2)	0.166(2)	6.9(9)
H12	0.287(3)	0.312(2)	0.201(1)	3.6(6)
H13	0.340(3)	0.444(2)	0.134(2)	6.6(9)
H14	0.129(3)	0.489(2)	0.081(1)	4.6(6)
H15	-0.052(3)	0.378(2)	0.106(2)	7.1(10)
H16	0.001(3)	0.370(2)	0.332(2)	5.6(7)
H17	0.240(3)	0.420(2)	0.332(1)	3.6(6)
H18	-0.118(3)	0.470(2)	0.246(2)	4.9(7)
H20	0.022(2)	0.589(2)	0.220(1)	3.6(6)
H26	0.886(2)	0.219(1)	0.306(1)	2.7(5)
H27	0.999(3)	0.255(2)	0.405(2)	5.6(8)
H28	0.944(3)	0.227(2)	0.505(2)	5.9(8)
H29	0.747(3)	0.151(2)	0.516(1)	4.6(6)
H30	0.638(3)	0.112(2)	0.407(2)	6.6(9)
H31	0.573(4)	0.327(3)	0.207(2)	7.8(11)
H32	0.417(7)	0.221(4)	0.143(3)	18.1(24)
H33	0.635(4)	0.166(3)	0.068(2)	10.6(13)
H34	0.863(6)	0.238(4)	0.114(3)	18.5(23)
H35	0.748(9)	0.289(5)	0.245(5)	26.6(38)
H37	0.374(3)	-0.018(2)	0.246(2)	5.2(7)
H38	0.266(3)	-0.121(2)	0.186(2)	5.4(8)
H39	0.313(4)	-0.150(3)	0.058(2)	7.3(10)
H40	0.511(2)	-0.097(2)	0.032(1)	3.7(6)
H41	0.611(2)	0.007(2)	0.094(1)	3.1(5)

Relevant bond distances and angles are presented in Table III and mean planes are listed in Table IV.

The cyclobutadiene group is square but not quite planar. If a plane is chosen through any three of the carbon atoms, the fourth one is 0.035 Å out of the plane. The bond distances in the C_4 ring average 1.462(5) Å[21] and the bond angles are very close to 90°.

The cyclopentadienyl ring bonded to cobalt is quite regular with an average carbon-carbon bond distance of 1.399(12) Å and an average bond angle of 107.5(5)°. This bond distance is in good agreement with similar average lengths in related compounds.[5,6,20] However it is somewhat, but perhaps not significantly shorter than corresponding average lengths in the cyclopentadienyl rings of the ferrocene moieties. These latter values are 1.411(6) Å for ring 1, 1.426(5) Å, ring 2; 1.426(4) Å, ring 3 and 1.411(2) Å for ring 4; where ring 1 is C1-C5; ring 2, C6-C10; ring 3, C11-C15 and ring 4, C16-C20.

Cobalt-carbon distances are normal, ranging from 1.973(2) Å to 2.012(1) Å, with an average of 1.986(5) Å, for the carbons in the cyclobutadiene ring and from 2.039(2) Å to 2.070(1) Å with an average of 2.058(5) Å for cyclopentadienyl carbons. The cobalt ring-centroid distances are 1.694 Å and 1.682 Å for the four and five membered rings, respectively. Iron-carbon bond distances were also quite regular with average values of 2.040(1) Å, 2.045(9) Å, 2.043(2) Å and 2.039(3) Å for rings 1, 2, 3 and 4, respectively. The corresponding ring centroid-iron distances are 1.653 Å, ring 1; 1.647 Å, Ring 2; 1.646 Å, ring 3; 1.642 Å, ring 4.

As has been observed with other cobalt-cyclobutadiene-cyclopentadiene sandwich compounds, the five and four membered rings are almost parallel, making a dihedral angle of 1.1°. The ferrocenyl groups are slightly below the four membered ring and point away from the cobalt atom (Table IV). They are also twisted to a small extent about the carbon-carbon bonds to the cyclobutadiene ring with the magnitude of the twist given by the torsion angles in Table III. A positive angle indicates clockwise rotation about the carbon-carbon bond when viewed from the cyclobutadiene ring outward. The ferrocenyl C_5 rings are in the eclipsed conformation and make dihedral angles with each other of 4.4° [Fe(1)] and 2.6° [Fe(2)]. The phenyl groups are also twisted about their bonds to the cyclobutadiene ring but to a much larger extent as seen from the magnitude of the torsion angles of 44.0° [C(36) - C(41)] and -57.6 [C(23) - C(28)] with the cyclobutadiene ring.

Bond distances and angles for the solvent molecule (not listed in the Tables) averaged 1.38 Å and 135° respectively. These values are not unreasonable when one considers the high thermal motion and disorder exhibited by the trapped solvent molecules. The analytical data did

TABLE III

Interatomic Distances (Å) and Angles (°)

Bond	Dist.	Bond	Dist.
Co-C(21)	1.984(1)	C(21)-C(22)	1.460(2)
-C(22)	1.973(2)	C(22)-C(23)	1.467(2)
-C(23)	1.975(1)	C(23)-C(24)	1.465(2)
-C(24)	2.012(1)	C(24)-C(21)	1.472(2)
-C(31)	2.070(2)	C(31)-C(32)	1.371(4)
-C(32)	2.064(2)	C(32)-C(33)	1.415(5)
-C(33)	2.039(2)	C(33)-C(34)	1.427(4)
-C(34)	2.055(2)	C(34)-C(35)	1.383(4)
-C(35)	2.064(2)	C(35)-C(31)	1.373(4)
Fe(1)-C(1)	2.040(2)	C(1)-C(2)	1.426(4)
-C(2)	2.041(2)	C(2)-C(3)	1.415(4)
-C(3)	2.040(2)	C(3)-C(4)	1.391(4)
-C(4)	2.040(2)	C(4)-C(5)	1.412(5)
-C(5)	2.037(2)	C(5)-C(1)	1.378(5)
-C(6)	2.058(2)	C(6)-C(7)	1.432(2)
-C(7)	2.074(1)	C(7)-C(8)	1.435(2)
-C(8)	2.043(2)	C(8)-C(9)	1.420(2)
-C(9)	2.024(2)	C(9)-C(10)	1.409(3)
-C(10)	2.028(2)	C(10)-C(6)	1.434(3)
Fe(2)-C(11)	2.046(2)	C(11)-C(12)	1.419(3)
-C(12)	2.052(2)	C(12)-C(13)	1.431(3)
-C(13)	2.040(2)	C(13)-C(14)	1.435(3)
-C(14)	2.040(2)	C(14)-C(15)	1.417(3)
-C(15)	2.039(2)	C(15)-C(11)	1.411(3)
-C(16)	2.039(2)	C(16)-C(17)	1.421(3)
-C(17)	2.031(2)	C(17)-C(19)	1.428(3)
-C(18)	2.046(2)	C(19)-C(20)	1.422(3)
-C(19)	2.043(2)	C(20)-C(18)	1.417(3)
-C(20)	2.038(2)	C(18)-C(16)	1.420(3)
C(25)-C(26)	1.393(2)	C(36)-C(37)	1.390(2)
C(26)-C(27)	1.383(2)	C(37)-C(38)	1.386(3)
C(27)-C(28)	1.373(3)	C(38)-C(39)	1.368(3)
C(28)-C(29)	1.381(3)	C(39)-C(40)	1.395(3)
C(29)-C(30)	1.383(3)	C(40)-c(41)	1.390(3)
C(30)-C(25)	1.388(2)	C(41)-C(36)	1.398(2)
C(21)-C(36)	1.465(2)		
C(22)-C(19)	1.462(2)		
C(23)-C(25)	1.472(2)		
C(24)-C(7)	1.447(2)		

(Continued)

TABLE III (Continued)

Bond Angles			
C(24)-C(21)-C(22)	89.8(1)	C(35)-C(31)-C(32)	108.8(3)
C(21)-C(22)-C(23)	90.4(1)	C(31)-C(32)-C(33)	107.6(3)
C(22)-C(23)-C(24)	89.8(1)	C(32)-C(33)-C(34)	107.6(2)
C(23)-C(24)-C(21)	90.0(1)	C(33)-C(34)-C(35)	105.8(3)
		C(34)-C(35)-C(31)	110.3(3)
C(10)-C(6)-C(7)	107.9(2)	C(15)-C(11)-C(12)	109.4(2)
C(6)-C(7)-C(8)	107.2(2)	C(11)-C(12)-C(13)	107.0(2)
C(7)-C(8)-C(9)	108.2(2)	C(12)-C(13)-C(14)	107.8(2)
C(8)-C(9)-C(10)	108.6(2)	C(13)-C(14)-C(15)	108.0(2)
C(9)-C(10)-C(6)	108.1(2)	C(14)-C(15)-C(11)	107.8(2)
C(18)-C(16)-C(17)	108.2(2)	C(5)-C(1)-C(2)	108.1(2)
C(16)-C(17)-C(19)	108.1(2)	C(1)-C(2)-C(3)	106.7(2)
C(17)-C(19)-C(20)	107.3(2)	C(2)-C(3)-C(4)	108.7(2)
C(19)-C(20)-C(18)	108.7(2)	C(3)-C(4)-C(5)	107.6(3)
C(20)-C(18)-C(16)	107.8(2)	C(4)-C(5)-C(1)	108.9(3)
C(41)-C(36)-C(37)	118.1(2)	C(26)-C(27)-C(28)	120.8(2)
C(36)-C(37)-C(38)	121.1(2)	C(27)-C(28)-C(29)	119.6(2)
C(37)-C(38)-C(39)	120.6(2)	C(28)-C(29)-C(30)	119.9(2)
C(38)-C(39)-C(40)	119.6(2)	C(29)-C(30)-C(25)	121.1(2)
C(39)-C(40)-C(41)	120.0(2)	C(30)-C(25)-C(26)	118.2(2)
C(40)-C(41)-C(36)	120.7(2)	C(25)-C(26)-C(27)	120.3(2)
C(21)-C(36)-C(37)	120.6(2)	C(24)-C(21)-C(36)	135.0(1)
C(21)-C(36)-C(41)	121.2(2)	C(22)-C(21)-C(36)	133.8(1)
C(22)-C(19)-C(17)	127.0(2)	C(21)-C(22)-C(19)	135.1(1)
C(22)-C(19)-C(20)	125.7(2)	C(23)-C(22)-C(19)	134.9(1)
C(23)-C(25)-C(26)	122.8(1)	C(22)-C(23)-C(25)	132.6(1)
C(23)-C(25)-C(30)	118.7(2)	C(24)-C(23)-C(25)	134.4(1)
C(24)-C(7)-C(8)	125.0(1)	C(23)-C(24)-C(7)	136.6(1)
C(24)-C(7)-C(6)	127.8(1)	C(21)-C(24)-C(7)	133.4(1)

Torsion Angles	
C(21)-C(24)-C(7)-C(6)	0.69
C(24)-C(23)-C(25)-C(30)	43.4
C(21)-C(22)-C(19)-C(17)	-4.1
C(22)-C(21)-C)36)-C(41)	-49.2

not reveal the presence of extra molecules because the crystals were crushed and vacuum dried in a pistol over boiling benzene.

A packing diagram of the unit cell contents (sans solvent molecules) is given in Figure 3. There are no intermolecular contacts of less than 3 Å.

TABLE IV

Mean Planes and Atomic Displacements (Å) Therefrom

A. Ring containing C(21), C(22), C(23), C(24)

$0.1260X + 0.7342Y - 0.6672Z = 1.4042$ $x^2 = 0.78$

C(21)	0.009(2)	C(7)	-0.019(2)
C(22)	-0.009(2)	C(19)	-0.261
C(23)	0.009(2)	C(25)	-0.316(2)
C(24)	-0.009(2)	C(36)	-0.195(2)
		Co	1.694

B. Cyclopentadiene rings

1. $0.1377X + 0.7231Y - 0.6769 = 1.9797$ $x^2 = 0.61$

C(31)	-0.006(3)	C(34)	-0.004(3)
C(32)	0.003(4)	C(35)	0.005(3)
C(33)	0.001(3)	Co	-1.682

2. $0.1834X + 0.6619Y - 0.7268Z = -5.1050$ $x^2 = 0.89$

C(1)	-0.001(2)	C(4)	0.003(3)
C(2)	0.002(2)	C(5)	-0.001(2)
C(3)	-0.003(2)	Fe	1.653

3. $0.1327X + 0.7083Y - 0.6933Z = 1.6154$ $x^2 = 0.56$

C(6)	0.000(2)	C(9)	0.003(2)
C(7)	0.002(2)	C(10)	-0.002(2)
C(8)	-0.003(2)	Fe	-1.647

4. $0.2847X - 0.4909Y - 0.8234 = 4.9416$ $x^2 = 0.33$

C(11)	0.005(2)	C(14)	0.005(2)
C(12)	0.002(2)	C(15)	-0.007(3)
C(13)	-0.002(2)	Fe	-1.646

5. $0.2442X - 0.5089Y - 0.8255Z = 8.4050$ $x^2 = 0.25$

C(16)	-0.002(2)	C(19)	-0.003(2)
C(17)	0.003(2)	C(20)	0.002(2)
C(18)	0.000(2)	Fe	1.642

C. Phenyl Rings

1. $0.5500X - 0.8346Y - 0.0323Z = 1.6778$ $x^2 = .83$

C(25)	0.008(2)	C(28)	0.002(2)
C(26)	-0.008(2)	C(29)	-0.002(2)
C(27)	0.003(2)	C(30)	-0.003(2)

2. $-0.5754X + 0.7211Y - 0.3860 = -4.2187$ $x^2 = 1.56$

C(36)	0.001(2)	C(39)	0.006(2)
C(37)	-0.003(2)	C(40)	-0.008(2)
C(38)	-0.001(2)	C(41)	0.004(2)

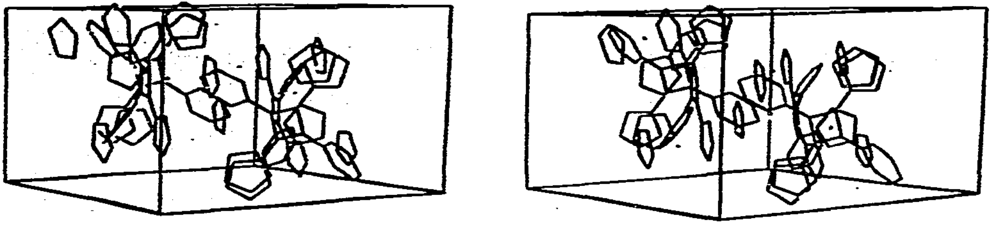

Fig. 3. Stereoscopic view of the unit cell illustrating the packing of compound 5. Solvent molecules are centered at 0 0 0 and 0 ½ ½.

EXPERIMENTAL SECTION

All melting points were taken in sealed capillaries under nitrogen and are uncorrected. CAMAG neutral alumina was used for column chromatography. (η^5-Cyclopentadienyl)dicarbonylcobalt,[18] ferrocenylphenylacetylene[7] and diferrocenylacetylene[7] were prepared according to literature methods. Elemental analyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Nmr spectra were recorded on a Varian A-60 instrument, ir spectra on a Beckman IR-10 instrument, and mass spectra on a Perkin-Elmer-Hitachi RMU-6L instrument at 70 eV. Skelly C is commercial heptane, b.p. 88-98°C.

Reaction of η^5-Cyclopentadienyldicarbonylcobalt and Ferrocenylphenylacetylene

A solution of 0.267 g (1.5 mmol) of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and 0.858 g (3.0 mmol) of ferrocenylphenylacetylene in 100 ml of degassed xylene was heated to reflux with magnetic stirring under a nitrogen atmosphere for 24 hr. The reaction mixture was allowed to cool under nitrogen, and the xylene was removed under reduced pressure until ca. 50 ml remained. The solution was filtered and added to a column of CAMAG neutral-grade alumina (deactivated with 5% H_2O) which had been packed in benzene. Elution with hexane-benzene removed an orange-red band, which after drying produced 0.814 g (78%) of a mixture of (η^5-cyclopentadienyl)(η^4-1,3-diferrocenyl-

2,4-diphenylcyclobutadiene)cobalt (5) and (η^5-cyclopentadienyl)(η^4-1,2-diferrocenyl-3,4-diphenylcyclobutadiene)cobalt (6). The products were separated by fractional crystallization from Skelly C.

The more symmetrical isomer (5) is the predominant product; it is appreciably less soluble than (6), and separates as dark red crystals, m.p. 207-208°C (Found: C, 70.59; H, 4.62; Co, 8.40; Fe, 16.00. $C_{41}H_{33}CoFe_2$ calcd.: C, 70.72; H, 4.78; Co, 8.46; Fe, 16.04%). The NMR spectrum in $CDCl_3$ exhibited peaks at τ 6.04 (10H, s, C_5H_5Fe), 5.88 (8H, m, C_5H_4Fe), 5.48 (5H, s, C_5H_5Co), 1.9-2.2, 2.4-2.8 (10H, m, C_6H_5). The mass spectrum exhibited the following principal peaks: m/e 696 (offscale, M^+), 631 (4, M - $C_5H_5^+$), 575 (4, M - $C_5H_5Fe^+$), 510 (10, M - $C_{10}H_{10}Fe^+$), 507 (13, M - $C_{10}H_{10}Co^+$), 410 (45, M - $C_{10}H_9FeC_2C_6H_5^+$), 344 (75, 410 - $C_5H_6^+$), 289 (100, 410 - $C_5H_5Fe^+$), 286 (60, $C_{10}H_9FeC_2C_6H_5^+$), 189 (55, $C_{10}H_{10}Co^+$), 186 (28, $C_{10}H_{10}Fe^+$), 124 (24, $C_5H_5Co^+$), 121 (36, $C_5H_5Fe^+$).

Later fractions produced the second isomer (6) as a microcrystalline orange solid, m.p. 199-200°C (Found: C, 70.69; H, 4.73; Fe, 15.99; Co, 8.78%). The NMR spectrum in $CDCl_3$ exhibited peaks at τ 6.05 (10H, s, C_5H_5Fe), 5.81 (4H, t, C_5H_4Fe), 5.67 (2H, M, C_5H_4Fe), 5.44 (2H, M, C_5H_5Fe), 5.40 (5H, s, C_5H_5Co), 2.3-2.5, 2.6-2.9 (10H, m, C_6H_5). The mass spectrum exhibited the following principal peaks: m/e 696 (offscale, M^+), 631 (5, M - $C_5H_5^+$), 575 (3, M - $C_5H_5Fe^+$), 518 (6, M - $C_6H_5C_2C_6H_5^+$), 510 (9, M - $C_{10}H_{10}Fe^+$), 507 (11, M - $C_{10}H_{10}Co^+$), 410 (30, M - $C_{10}H_9FeC_2C_6H_5^+$), 394 (5, $C_{10}H_9FeC_2C_{10}H_9Fe^+$), 344(36, 410 - $C_5H_6^+$), 302 (8, M - $C_{10}H_9FeC_2C_{10}H_9Fe^+$), 289 (100, 410 - $C_5H_5Fe^+$), 286 (18, $C_{10}H_9FeC_2C_6H_5^+$), 189 (30, $C_{10}H_{10}Co^+$), 186 (23, $C_{10}H_{10}Fe^+$), 178 (9, $C_6H_5C_2C_6H_5^+$), 124 (15, $C_5H_5Co^+$), 121 (38, $C_5H_5Fe^+$).

Continued elution with benzene removed a dark band which produced a very small amount of a purple solid. The mass spectrum of this material exhibited an intense molecular ion peak at m/e 724, weaker peaks in the high mass region at m/e 659 and 538 corresponding to M - $C_5H_5^+$ and M - $C_{10}H_{10}Fe^+$ ions, respectively, etc. On this basis, the purple product is tentatively identified as one or more of the isomeric complexes

(η^5-cyclopentadienyl)(η^4-diferrocenyldiphenylcyclopentadienone)cobalt.

Reaction of η^5-Cyclopentadienyldicarbonylcobalt and Diferrocenylacetylene

In a manner similar to that described above, a mixture of 0.267 g (1.5 mmol) of (η^5-C_5H_5)Co$(CO)_2$) and 1.182 g (3.0 mmol) of diferrocenylacetylene in 100 ml of degassed xylene was heated to reflux under nitrogen for 24 hr. Column chromatography of the reaction mixture on alumina and elution with benzene afforded 1.13 g (83%) of (η^5-cyclopentadienyl)-(η^4-tetraferrocenylcyclobutadiene)cobalt (4). An analytical sample was prepared by a subsequent crystallization of a portion of the product from methylene chloride/hexane, orange-brown crystals, m.p. 279-281°C (Found: C, 64.90; H, 4.85; Co, 6.40; Fe, 24.02. $C_{49}H_{41}CoFe_4$ calcd.: C, 64.52; H, 4.53; Co, 6.46; Fe, 24.41%). The NMR spectrum in $CDCl_3$ exhibited peaks at τ 5.90 (20H, s, C_5H_5Fe), 5.70 (8H, t, beta-C_5H_4Fe), 5.23 (5H, s, C_5H_5Co), and 5.20 (8H, t, alpha-C_5H_4Fe). The mass spectrum exhibited the following principal peaks: m/e 912 (offscale, M^+), 788 (22, M - $C_5H_5Co^+$), 518 (80, M - $C_{10}H_9FeC_2C_{10}H_9Fe^+$), 189 (80, $C_{10}H_{10}Co^+$), 186 (100, $C_{10}H_{10}Fe^+$), 124 (71, C_5H_5Co), 121 (80, $C_5H_5Fe^+$).

Crystallographic Studies

Crystals suitable for X-ray studies were grown from benzene-hexane mixtures. Preliminary examination by precession and Weissenberg film methods showed that the crystals are monoclinic $P2_1/c$ (systematic absences $h0\ell$ with ℓ odd and 0k0 with k odd). The crystal used for data collection was almost a rectangular parallelepiped of dimensions 0.5 x 0.5 x 0.6 mm^3. It was mounted with the long dimension (a axis) roughly parallel to the ϕ axis of a CAD-4 computer controlled 4-circle diffractometer (Enraf-Nonius). Cell dimensions were determined from 25 accurately centered reflections by a least squares technique. The results were a = 10.551(3), b = 16.345(2), c = 19.796(3) Å, and β = 93.19(1)°, V = 3408(2) $Å^3$. Assuming Z = 4, the calculated density is 1.362 g/cm^{-3} as compared to a measured density (flotation in CH_2Cl_2-C_2H_5Br mixture) 1.44(2) g/cm^{-3}. However, with inclusion of the solvent molecule the calculated density is 1.441 g/cm^{-3}.

Intensity data were collected by the θ-2θ scan technique out to a value of $2\theta_{max}$ = 70° with monochromatized (graphite crystal) MoKα (λ = 0.7107 Å) radiation at a 4° take-off angle. The scan rate was variable ranging from 20°/min for the strongest reflections to 2.0°/min for the weakest. The angular scan width was also variable and amounted to 3X (0.65 + 0.2 tan θ). Right and left backgrounds were each scanned for 25% of the time required for the total peak scan. Three intensity control reflections were recorded every time a set of 60 reflections was collected. The fluctuation in intensity of this standard was random with a deviation about the mean amounting to no more than ±3%. A total of 10,450 reflections were scanned in the hkl and hk$\bar{l}$ octants. Of these 7315 were found to have intensities equal to or greater than 3σ, where $\sigma = [\text{Total Counts} + \text{Bkgd Counts} + (pI)^2]^{1/2}$, and therefore considered to be observed. In this equation p was chosen as equal to 0.05. The intensities were corrected for Lorentz and double polarization[22] effects and also for absorption.[2] Since μ = 13.94 cm^{-1} calculated transmission factors ranged from 0.57 to 0.27.

Solution and Refinement of the Structure.- The structure was solved by a straightforward application of the Σ_2 relationship[23] in a symbolic-addition procedure.[24] The programs used were those of Ahmed.[25] Phases for 280 reflections were uniquely defined and an E map prepared from them gave the positions of all the metal atoms. Subsequent Fourier and difference maps revealed the presence of all the remaining atoms in molecule (5) including hydrogens. After several cycles of full-matrix least squares refinement (anisotropic for all non-hydrogen atoms), a difference map revealed the presence of several peaks with electron densities of the order of 2-3 e/A^3. Their high thermal parameters and location between molecules of (5) indicated a solvent molecule. Three major peaks were represented as carbon atoms and these bonded through C_{44} to a symmetry related carbon to create a six carbon chain (probably hexane). Refinement then proceeded smoothly until the shifts in the parameters were ~0.1 (~0.2 for hydrogens) of their standard deviations.[26] The final value of $R(F) = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$ was 0.039 and of the weighted residual, $Rw(F) = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{\frac{1}{2}}$, 0.058. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ with weights, w, assigned by the expression $w = \frac{1}{\sigma^2(F_o)}$ and $\sigma(F_o{}^2) = \left[\sigma(I)^2 + (0.05F^2)^2\right]^{\frac{1}{2}}/LP$. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber[27] and were corrected for anomalous dispersion (both real and imaginary parts). Scattering factors for hydrogen were taken from Stewart, et al.[28]

The final difference Fourier was featureless with a number of peaks of height $<\pm 0.3 eA^{-3}$ distributed randomly throughout the map.

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21. The numbers in parenthesis following average values in the text are standard deviations of the mean calculated as

$$\sigma = \left[\frac{(X_i - \bar{X})^2}{n(n-1)}\right]^{\frac{1}{2}}$$

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26. The programs used in this work unless otherwise stated were either those of F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Huber, NRC Crystallographic programs for the IBM 360, Division of Pure Physics, National Research Council, Ottawa, Canada, 1968 or Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975.

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