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STUDIES ON THE INTERACTIONS OF (η^5-C_5H_5)M(CO)$_2$ COMPLEXES (M = Co, Rh) WITH 1,2-BIS(PHENYLETHYNYL)BENZENE, AND AN X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF ONE OF THE PRODUCTS: (η^5-$C_5H_5Co)_2(C_6H_5C_2C_6H_4C_2C_6H_5)_2$

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Summary

The reaction of (η^5-C_5H_5)Co(CO)$_2$ (1) and 1,2-bis(phenylethynyl)benzene (4) has been shown to produce as major products a dimeric organic compound of composition $C_{44}H_{28}$, postulated to be 1,2,4-triphenyl-3-(*o*-phenylethynylphenyl)biphenylene (7), and bis(η^5-$C_5H_5Co)_2(C_6H_5C_2C_6H_4C_2C_6H_5)_2$ (9). Minor organometallic products also obtained include a bis(η^4-cyclopentadienone)dicobalt complex (12) and several mononuclear complexes resulting from co-condensation of 4 and 7 with 1. A corresponding reaction between (η^5-C_5H_5)-Rh(CO)$_2$ (2) and 4 has produced several organorhodium complexes in low yield, including a mixed (η^4-cyclobutadiene)(η^4-cyclopentadienone)dirhodium derivative (17). Complexes 9, 12 and 17 are derived from the intermolecular condensation of two molecules of 4 with either 1 or 2. An X-ray diffraction investigation of 9 has been undertaken, and unequivocally confirms the unique structural nature of this complex to be that of the b isomer.

9b crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions: a = 10.652(5), b = 23.690(6), c = 17.204(4) Å, and β = 90.21(3)°; V = 4341(4) Å^3. The unit cell was found to contain one solvent benzene for each molecule, yielding a calculated density of 1.351(1) g/cm^3 with Z = 4. Intensity data were collected using Mo-K_α radiation (λ = 0.71073 Å) by the θ—2θ scan method with an automated 4-circle diffractometer (Enraf-Nonius CAD-4). In all, 8286 reflections were scanned, of which 5192 were independent with an intensity greater than 3σ. Refinement by full matrix least squares led to a final unweighted R of 0.037 (R_w = 0.050). The atoms of the (η^5-C_5H_5)Co(C_4) moieties are well-behaved

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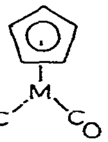
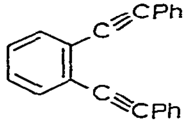
crystallographically and have molecular parameters which are within accepted values of recent determinations of other complexes containing that moiety.

Introduction

Since the pioneering work of Hubel and coworkers, studies relating to the interactions of acetylenes and metal carbonyls have provided a vast array of organic and organometallic products, many of which possess unusual structures, bonding features and spectral properties [1]. In 1967, it was demonstrated in one of our laboratories that the reaction of η^5-cyclopentadienyldicarbonylcobalt (1) and diphenylacetylene in refluxing aromatic solvents produced η^4-cyclobutadiene- and η^4-cyclopentadienone-cobalt complexes as well as hexaphenylbenzene, a product of cyclic trimerization of diphenylacetylene [2]. Since that time, additional studies on reactions of diphenylacetylene with η^5-cyclopentadienyldicarbonylrhodium (2) and -iridium (3) have uncovered a variety of novel metallocyclic, binuclear and trinuclear metal-cluster complexes, some of which exhibit fluxional behavior [3—5].



(1, M = Co;
2, M = Rh;
3, M = Ir)



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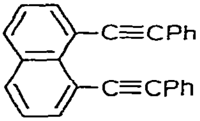

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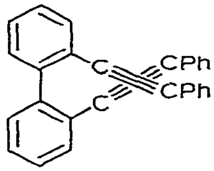


(6)

In contrast to mono-acetylenes, reactions of diacetylenes, especially aromatic diacetylenes, with metal carbonyls have been considerably less studied. It has therefore been of interest to us to investigate reactions of the acyclic diacetylenes 1,2-bis(phenylethynyl)benzene (4), 1,8-bis(phenylethynyl)naphthalene (5), and 2,2'-bis(phenylethynyl)biphenyl (6) with $(\eta^5\text{-}C_5H_5)M(CO)_2$ derivatives, since the geometries afforded by the two acetylenic units for bonding to the metal would vary significantly, and might be expected to produce products derived from either intra- or intermolecular interactions [6].

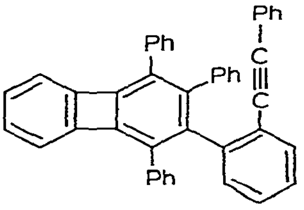
In this paper, we present findings relating to the reactions of $(\eta^5\text{-}C_5H_5)M(CO)_2$, complexes 1 and 2 with the diacetylene 4, and also the results of a single-crystal X-ray diffraction study on one of the novel binuclear products, $(\eta^5\text{-}C_5H_5Co)_2\text{-}(C_6H_5C_2C_6H_4C_2C_6H_5)_2$ (9).

Results and discussion

Synthesis and spectral considerations

The interaction of equimolar amounts of 1 and 4 in refluxing xylene has produced one organic and four organometallic complexes, all of which could be separated and purified by standard chromatographic and crystallization techniques. The organic product was isolated as light yellow crystals in 25% yield. The mass spectrum and elemental analysis of this product clearly indicate that it has the composition $C_{44}H_{28}$ and is therefore a dimeric species derived from two molecules of 4. In addition to the molecular ion at *m/e* 556, which is also the base peak, major fragment ions at *m/e* 479, 402 and 325 are observed which correspond to losses of one, two and three phenyl substituents, respectively. A peak at *m/e* 379 can likewise be assigned to loss of a phenylethynylphenyl substituent from the molecular ion.

A reasonable structural assignment for the organic product is 1,2,4-triphenyl-3-(*o*-phenylethynyl-phenyl)biphenylene (7), since such a product might be anticipated to result from the dimerization of two molecules of 4, utilizing two acetylenic linkages from one molecule and one from the second molecule. Although a definitive acetylenic stretching frequency could not be observed in the infrared spectrum of 7, it is known that in closely related structures of this type, the acetylenic absorption is either absent or so weak that it is very difficult to observe [7]. In any event, the only other known dimeric derivative of 4, 1,2-diphenyl-3-[*o*-phenylethynyl-phenyl]-4-phenylethynylazulene (8), can be ruled out as a structure for the organic product on the basis of its melting point, spectral properties and color [7]. Other azulenic structures previously proposed for this dark green $C_{44}H_{28}$ hydrocarbon [8,9] can likewise be eliminated on this latter basis.



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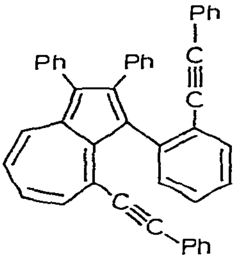


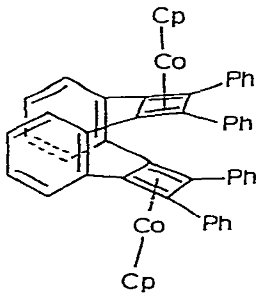
(8)

The principal organometallic product (33%) arising from the interaction of 1 and 4 was a high melting, crystalline material whose proton NMR spectrum exhibited a single sharp resonance at τ 5.42 as well as multiplet absorption in the aromatic region. Total elemental analyses and the mass spectra of the product again clearly indicated a dimeric formulation, corresponding in this case to the composition $(C_5H_5)_2Co_2(C_6H_5C_2C_6H_4C_2C_6H_5)_2$. In addition to an intense molecular ion at *m/e* 804, indicating the high stability of the product, fragmentation peaks at *m/e* 680 and 556, corresponding to losses of one and two C_5H_5Co moieties, respectively, were also observed.

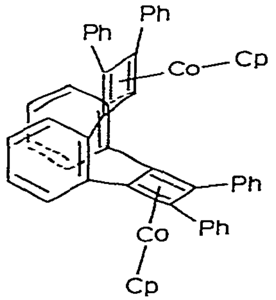
On the basis of the above data, a tentative structural formulation for the product as a bis-(η^4-cyclobutadiene) complex (**9**) was indicated. A somewhat related structure (**10**) has previously been proposed for the product resulting from the interaction of **4** and palladium dichloride in benzene [10]. In addition, a binuclear condensation product (**11**) containing both metallocyclic and η^4-cyclobutadiene rings has been isolated from reactions between **4** and iron carbonyls [11]. The unique structural nature of **11** was subsequently elucidated by means of an X-ray crystallographic investigation [12].

The unusual molecular arrangements in all three complexes **9**—**11** are derived from the intermolecular condensation of two molecules of **4** with a metal or organometal fragment, and result in bis(η^4-cyclobutadiene)dimetal, bis(η^4-cyclobutadiene)metal and (η^4-cyclobutadiene)(η^4-metallocycle)metal derivatives, respectively. Because of the unique nature of **9** and its possible relationship to other complexes such as **10** and **11**, as well as to products derived from interactions of **1** with mono-acetylenes, an X-ray crystallographic structural investigation was undertaken to determine which isomer had been formed (vide infra).

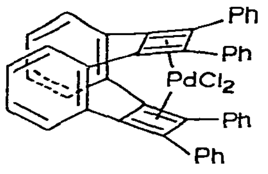
In addition to **9**, a deep red product which appears to be structurally related to **9** was isolated in very low yield. The proton NMR spectrum of the product contained, in addition to a multiplet aromatic resonance, a singlet in the η^5-C_5H_5Co region at τ 4.90, somewhat deshielded compared to the singlet representing the η^5-C_5H_5Co protons in **9**. A very intense, broad absorption in the infrared spectrum of the product near 1590 cm^{-1} is consistent with a metal-coordinated cyclopentadienone ring. The mass spectrum of the product exhibited an intense molecular ion at *m/e* 860, as well as major fragment peaks assignable to (M — CO) (832), (M — C_5H_5Co) (736), ($C_{22}H_{14}$) (278), ($C_{10}H_{10}Co$) (189) and (C_5H_5Co) (124) ions. On the basis of this data, the product can tentatively be assigned as the bis(η^4-cyclopentadienone)dicobalt complex **12a** or **12b**.



(9a)



(9b)



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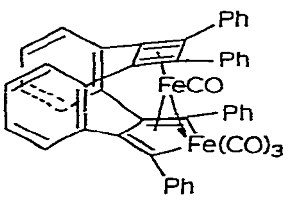

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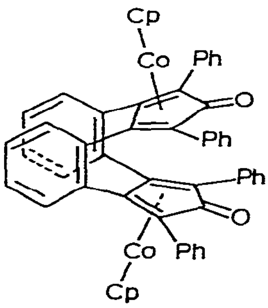
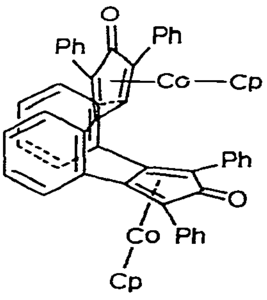
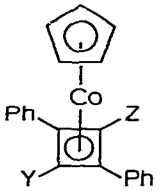


(12 a)

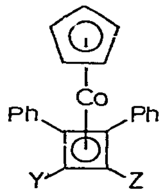


(12 b)

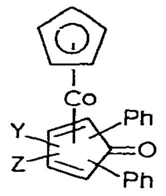
Two other organometallic products were also isolated in very small amounts from this reaction, and appear to be the mononuclear (η^4-cyclobutadiene)cobalt and (η^4-cyclopentadienone)cobalt complexes 13 and 14, respectively, on the basis of data presently available. They may be considered to be derived from the condensation of one molecule each of 4 and the dimeric product 7 with 1, and in fact there are many similarities between the infrared spectra of 13 and 14 with that of 7. Complex 13 has been characterized by total elemental analysis and by mass spectrometry ($M^+ = 958$). The appearance of two closely related η^5-C_5H_5Co resonances in the proton NMR spectrum of 13 is possibly due to the presence of two structural isomers (**13a**, **13b**) [6,13]. Further, 14 exhibits a molecular ion at *m/e* 986, and the fact that a series of η^5-C_5H_5Co resonances are observed for the product suggests the presence of several structural isomers of this substituted η^4-cyclopentadienonecobalt complex, as was also observed in earlier studies [13].



(13a)

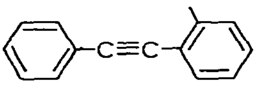


(13b)

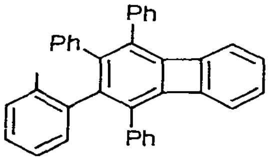


(14)

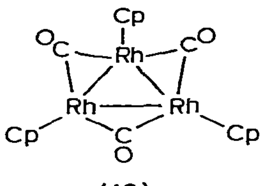
Y =



Z =

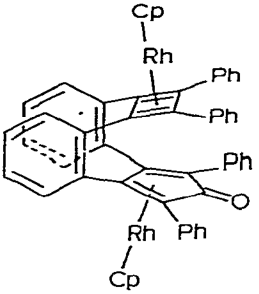


The interaction of equimolar amounts of the rhodium analog 2 and 4 in refluxing xylene likewise afforded the organic dimerization product 7 as well as several organometallic products in low yields. One such product, a dark green solid (15), has the composition $(\eta^5\text{-}C_5H_5Rh)_3\text{-}(C_6H_5C_2C_6H_4C_2C_6H_5)_2$ on the basis of elemental analysis and mass spectrometry ($M^+ = 1060$). The proton NMR spectrum of 15 is unique in that it contains three distinct η^5-C_5H_5Rh resonances at τ 5.13, 5.27 and 5.40. Further structural characterization of this product, which may be fluxional in nature on the basis of related studies [4,5], is currently in progress. A low yield of the known [14] trinuclear complex $(\eta^5\text{-}C_5H_5Rh)_3\text{-}(\mu\text{-}CO)_3$ (16) was also obtained in this reaction.

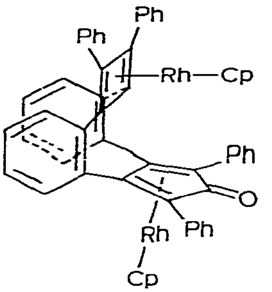


(16)

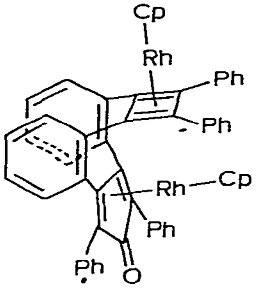
The final product to be isolated from the reaction of 2 and 4 is assigned as the mixed (η^4-cyclobutadiene)(η^4-cyclopentadienone)dirhodium complex 17 on the basis of elemental analysis, mass spectrometry ($M^+ = 920$), a strong absorption attributed to a coordinated cyclopentadienone ring in the infrared spectrum near 1590 cm^{-1}, and two non-equivalent η^5-C_5H_5Rh singlets of equal intensity at τ 4.72 and 5.35 in the proton NMR spectrum. As in the case of the binuclear cobalt complexes 9 and 12 as well as the palladium and iron complexes 10 and 11, the mixed ring dirhodium complex 17 may be regarded as being derived from the intermolecular condensation of two molecules of 4 with a metal or organometal species, in this instance two molecules of 2. The formation of 17 thus represents yet another unique manner in which this condensation process may occur.



(17a)



(17b)



(17c)

Crystallographic considerations

A single crystal X-ray diffraction study of compound 9 revealed that isomer b was the isolated product. Figure 1 is an ORTEP drawing of the molecule [16] and includes the atom numbering scheme used in the tables. Selected bond lengths are presented in Table 1 and bond and torsion angles in Table 2. Generic parts of the molecule are labelled according to which cobalt atom they are attached. Thus, Cp(1) represents the cyclopentadienyl group (C(1) to C(5)) and Cb(1) the cyclobutadienyl group (C(11) to C(14)) bonded to Co(1). The phenyl rings are labelled as follows: Ph(1) (C(31) to C(36)), Ph(2) (C(37) to C(42)), Ph(3) (C(43) to C(48)) and Ph(4) (C(49) to C(54)).

The bond lengths and angles of the (η^5-C_5H_5)Co(η^4-C_4) fragments in 9b are typical of those in other complexes [17]. The cyclobutadiene rings are planar (Table 3) and regular with bond lengths ranging from 1.460(4) to 1.477(4) Å and averaging 1.468(4) Å. Bond angles in both rings are 90° within 3 standard deviations. The cyclopentadienyl rings are also planar but the bond distances in Cp(1) are significantly smaller than those in Cp(2) (Ave. C—C = 1.368(8) Å for Cp(1) and 1.405(4) Å for Cp(2)). This is partly due to the higher thermal motion of Cp(1) and possibly to some steric crowding from the phenyl groups on Cb(2). Bond angles average 108.0(5)° in both cyclopentadienyl rings. The cobalt—carbon bond distances are typical with average values of 2.041(5) Å for Co(1)—C(Cp(1)), 2.064(4) Å for Co(2)—C(Cp(2)), 1.986(3) Å for Co(1)—C(Cb(1)) and 1.985(8) Å for Co(2)—C(Cb(2)). The cobalt-to-ring centroid distances are 1.677 Å (Co(1)—Cp(1)), 1.683 Å (Co(2)—Cp(2)), 1.694 Å

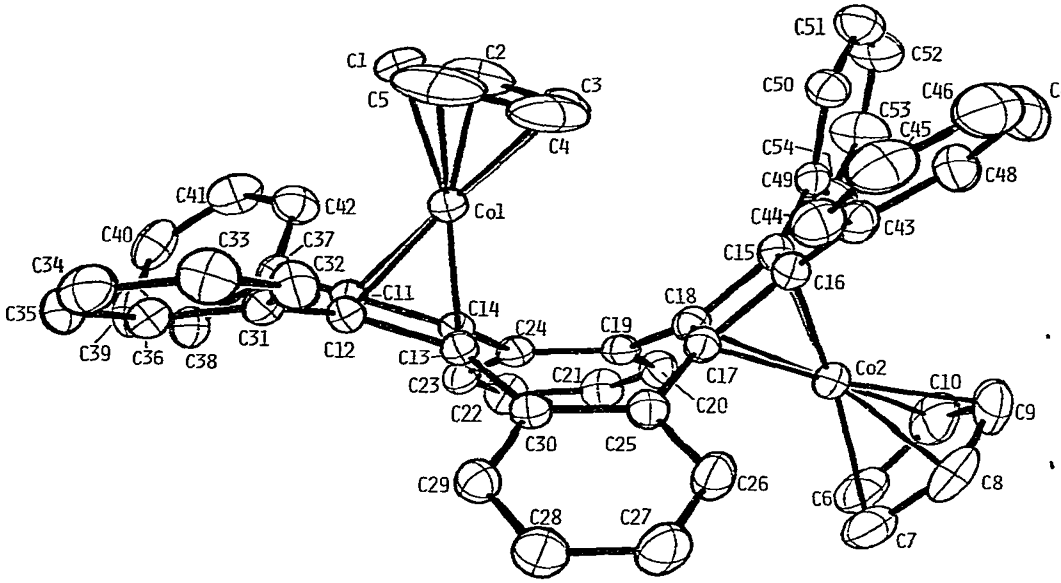
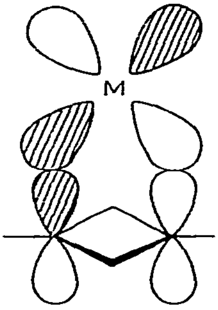


Fig. 1. Molecular structure of **9b** showing the numbering scheme used in the text and tables. Hydrogens are omitted for clarity but are numbered according to the carbon atoms to which they are attached. Thermal ellipsoids are at the 40% probability level.

(Co(1)—Cb(1)) and 1.691 Å (Co(2)—Cb(2)). The four- and five-membered rings bonded to the same cobalt atoms are nearly parallel, having dihedral angles of 3.2° and 2.4° for the rings on Co(1) and Co(2), respectively (Table 3).

The terminal phenyl groups are all planar and displaced out of the cyclobutadiene planes away from the cobalt atoms (see Table 3). These groups also twist with respect to the C_4 rings from 29.1° for Ph(1) to 52.5° for Ph(2). The bridging six-membered rings are distorted slightly from planarity but the bond distances and angles are regular. Like the terminal phenyls, these bridging rings are displaced out of the Cb planes away from the metal atoms. These rings are also twisted by different amounts relative to the two C_4 rings. This arrangement of bridging phenyl groups between the two cyclobutadienyl rings takes the form of an eight membered ring with boat conformation.

The displacement of substituents out of the cyclobutadiene plane away from the metal is a common feature in all of the complexes studied thus far (see Table 1 of ref. 17) and is a consequence of the electronic interactions between the cyclobutadiene ring and metal, rather than to any steric repulsions between the Cb substituents. Both extended Hückel calculations [18] and theoretical deformation density studies using the Fenske-Hall technique [19] have demonstrated that the Cb *e* orbitals in **18** rehybridize to **19** in order to maximize the overlap with the metal *e* set (d_{xz} and d_{yz} orbitals) and strengthen the M—C(Cb) bond. This rehybridization leads to the tilting of the C(Cb)—R linkage and the displacement of the R group out of the ring plane away from the metal. Such tilting forces the substituents closer together, thereby increasing their steric repulsions. To relieve these stresses, the C(Cb)—C(Cb) bond lenthens and the substituents twist. One additional consequence of these distortions is that little conjugation results between the four- and six-membered rings, as evidenced by the C(Cb)—C(R) mean distance of 1.470(2) Å for **9b**. This is near the value of 1.487(6) Å found by Allmann and Helmer [20] for the C(sp^2)—C(sp^2) single bond.



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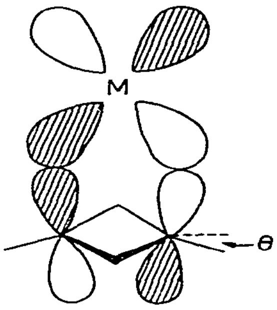

(19)

TABLE 1

INTERATOMIC DISTANCES (Å)

Bond	Distance	Bond	Distance
Co(1)—C(1)	2.042(3)	Co(2)—C(6)	2.065(3)
Co(1)—C(2)	2.057(4)	Co(2)—C(7)	2.078(3)
Co(1)—C(3)	2.042(4)	Co(2)—C(8)	2.060(3)
Co(1)—C(4)	2.029(4)	Co(2)—C(9)	2.052(3)
Co(1)—C(5)	2.036(4)	Co(2)—C(10)	2.066(3)
Co(1)—C(11)	1.990(3)	Co(2)—C(15)	1.966(3)
Co(1)—C(12)	1.994(3)	Co(2)—C(16)	1.979(3)
Co(1)—C(13)	1.979(3)	Co(2)—C(17)	2.003(3)
Co(1)—C(14)	1.982(3)	Co(2)—C(18)	1.992(3)
C(1)—C(2)	1.353(6)	C(6)—C(7)	1.391(5)
C(2)—C(3)	1.351(6)	C(7)—C(8)	1.405(5)
C(3)—C(4)	1.377(7)	C(8)—C(9)	1.419(5)
C(4)—C(5)	1.395(7)	C(9)—C(10)	1.405(5)
C(5)—C(1)	1.362(6)	C(10)—C(6)	1.407(5)
C(11)—C(12)	1.460(4)	C(15)—C(16)	1.467(4)
C(12)—C(13)	1.476(3)	C(16)—C(17)	1.470(4)
C(13)—C(14)	1.465(4)	C(17)—C(18)	1.460(4)
C(14)—C(11)	1.469(3)	C(18)—C(15)	1.477(4)
C(11)—C(37)	1.485(4)	C(15)—C(49)	1.466(4)
C(12)—C(31)	1.463(4)	C(16)—C(43)	1.467(4)
C(13)—C(30)	1.467(4)	C(17)—C(25)	1.470(4)
C(14)—C(24)	1.469(4)	C(18)—C(19)	1.471(4)
C(19)—C(20)	1.387(4)	C(25)—C(26)	1.403(4)
C(20)—C(21)	1.383(4)	C(26)—C(27)	1.371(4)
C(21)—C(22)	1.376(4)	C(27)—C(28)	1.386(4)
C(22)—C(23)	1.376(4)	C(28)—C(29)	1.367(4)
C(23)—C(24)	1.394(4)	C(29)—C(30)	1.397(4)
C(24)—C(19)	1.413(4)	C(30)—C(25)	1.409(4)
[C—C(Ph(1))] [a]	1.383(5)	[C—C(Ph(3))]	1.386(5)
[C—C(Ph(2))]	1.382(3)	[C—C(Ph(4))]	1.379(6)

[a] Bracketed quantities are those for which a mean value has been calculated.

Standard deviations from the mean were calculated as $\bar{\sigma} = \left[\frac{\sum_{i}^{n}(\bar{X} - X_i)^2}{n(n-1)}\right]^{1/2}$ where $\bar{X} = \sum_{i}^{n} X_i/n$.

TABLE 2

INTERATOMIC ANGLES (deg) AND TORSION ANGLES FOR COMPOUND 9b

Atoms	Angle	Atoms	Angle
[C(Cp(1))—Co(1)—C(Cp(1))] [a]	39.1(3)	[C(Cp(2))—Co(2)—C(Cp(2))]	39.8(2)
[C(Cb(1)—Co(1)—C(Cb(1))]	43.4(1)	[C(Cb(2))—Co(2)—C(Cb(2))]	43.4(2)
[C—C—C(Cp(1))]	108.0(5)	[C—C—C(Cp(2))]	108.0(4)
C(14)—C(11)—C(12)	90.5(2)	C(18)—C(15)—C(16)	89.5(2)
C(11)—C(12)—C(13)	89.7(2)	C(15)—C(16)—C(17)	90.2(2)
C(12)—C(13)—C(14)	90.0(2)	C(16)—C(17)—C(18)	90.1(2)
C(13)—C(14)—C(11)	89.8(2)	C(17)—C(18)—C(15)	90.2(2)
C(14)—C(11)—C(37)	131.6(2)	C(18)—C(15)—C(49)	134.9(2)
C(12)—C(11)—C(37)	137.0(2)	C(16)—C(15)—C(49)	133.9(2)
C(11)—C(12)—C(31)	136.6(2)	C(15)—C(16)—C(43)	135.4(2)
C(13)—C(12)—C(31)	133.7(2)	C(17)—C(16)—C(43)	133.7(2)
C(12)—C(13)—C(30)	132.2(2)	C(16)—C(17)—C(25)	133.3(2)
C(14)—C(13)—C(30)	134.6(2)	C(18)—C(17)—C(25)	136.6(2)
C(13)—C(14)—C(24)	137.4(2)	C(17)—C(18)—C(19)	135.7(2)
C(11)—C(14)—C(24)	130.8(2)	C(15)—C(18)—C(19)	133.6(2)
C(14)—C(24)—C(19)	124.5(2)	C(18)—C(19)—C(24)	122.6(2)
C(13)—C(30)—C(25)	123.3(2)	C(17)—C(25)—C(30)	122.8(2)
C(14)—C(24)—C(23)	116.9(2)	C(18)—C(19)—C(20)	119.5(2)
C(13)—C(30)—C(29)	118.0(2)	C(17)—C(25)—C(26)	119.0(2)
C(24)—C(19)—C(20)	117.9(2)	C(30)—C(25)—C(26)	118.2(2)
C(19)—C(20)—C(21)	122.7(3)	C(25)—C(26)—C(27)	121.9(3)
C(20)—C(21)—C(22)	119.1(3)	C(26)—C(27)—C(28)	119.4(3)
C(21)—C(22)—C(23)	119.6(3)	C(27)—C(28)—C(29)	119.9(3)
C(22)—C(23)—C(24)	122.1(3)	C(28)—C(29)—C(30)	121.9(3)
C(23)—C(24)—C(19)	118.6(2)	C(29)—C(30)—C(25)	118.6(2)
[C—C—C(Ph(1))]	120.0(7)	[C—C—C(Ph(3))]	119.9(3)
[C—C—C(Ph(2))]	120.0(4)	[C—C—C(Ph(4))]	120.0(6)
Torsional angles [b]			
C(11)—C(14)—C(24)—C(23)	—23.5	C(15)—C(18)—C(19)—C(20)	51.9
C(11)—C(14)—C(24)—C(19)	156.8	C(15)—C(18)—C(19)—C(24)	—126.3
C(12)—C(13)—C(30)—C(29)	23.2	C(16)—C(17)—C(25)—C(26)	—52.7
C(12)—C(13)—C(30—C(25)	—159.3	C(16)—C(17)—C(25)—C(30)	124.8
C(13)—C(30)—C(25)—C(17)	1.6	C(11)—C(12)—C(31)—C(32)	—150.9
C(14)—C(24)—C(19)—C(18)	0.2	C(12)—C(11)—C(37)—C(38)	—52.5
C(24)—C(14)—C(13)—C(30)	—3.4	C(15)—C(16)—C(43)—C(44)	149.3
C(19)—C(18)—C(17)—C(25)	5.1	C(16)—C(15)—C(49)—C(50)	—31.7

[a] See footnote to Table 1. [b] In the series of atoms A—B—C—D, a positive angle represents the clockwise rotation of D relative to A about the B—C bond.

Bond distances and angles for the solvent molecule averaged 1.33(6) Å and 120(3)° (planar within the high thermal motion) and confirmed the solvent as benzene. The analytical data did not reveal the presence of extra molecules because the crystals were crushed and vacuum dried.

A packing diagram of the unit cell contents is shown in Fig. 2. There are no close intermolecular contacts except for several H—H interactions [H(29)—H′(36) = 2.35 Å, H(28)—H′(39) = 2.41 Å, H(8)—H′(27) = 2.55 Å, where H atoms are in symmetry positions xyz and H′ atoms are in $\bar{x}\bar{y}\bar{z}$]. There are also several close H—H intramolecular contacts as shown in Table 4.

TABLE 3

LEAST-SQUARES PLANES [a] WITH DEVIATIONS OF ATOMS FROM THESE PLANES (in Å) FOR COMPOUND 9b

A. Cyclopentadienyl ring 1: C(1), C(2), C(3), C(4), C(5)			
$0.7172X + 0.6292Y - 0.2995Z = -9.1622$			$\chi^2 = 1$
C(1)	−0.001(4)	C(4)	−0.002(5)
C(2)	0.000(4)	C(5)	0.002(4)
C(3)	0.001(4)	Co(1)	−1.677(0)
B. Cyclopentadienyl ring 2: C(6), C(7), C(8), C(9), C(10)			
$-0.6905X - 0.2710Y - 0.6706Z = -3.5548$			$\chi^2 = 1$
C(6)	−0.002(4)	C(9)	−0.002(4)
C(7)	0.001(4)	C(10)	0.002(4)
C(8)	0.000(4)	Co(2)	−1.683(0)
C. Cyclobutadiene ring 2: C(11), C(12), C(13), C(14)			
$0.6771X + 0.6613Y - 0.3229Z = -5.7220$			$\chi^2 = 0$
C(11)	0.001(3)	Co(1)	1.694(0)
C(12)	−0.001(3)	C(24)	−0.277(3)
C(13)	0.001(3)	C(30)	−0.347(3)
C(14)	−0.001(3)	C(31)	−0.018(3)
		C(37)	−0.179(3)
D. Cyclobutadiene ring 2: C(15), C(16), C(17), C(18)			
$-0.6993X - 0.3043Y - 0.6468Z = 0.1265$			$\chi^2 = 1$
C(15)	0.002(3)	Co(2)	1.691(0)
C(16)	−0.002(3)	C(19)	−0.136(3)
C(17)	0.002(3)	C(25)	−0.037(3)
C(18)	−0.002(3)	C(43)	−0.172(3)
		C(49)	−0.240(3)
E. Bridging phenyl ring 1: C(19), C(20), C(21), C(22), C(23), C(24)			
$-0.4319X - 0.8887Y - 0.1537Z = 4.0417$			$\chi^2 = 55$
C(19)	0.009(3)	C(22)	0.008(4)
C(20)	0.004(3)	C(23)	0.008(3)
C(21)	−0.015(4)	C(24)	−0.014(3)
F. Bridging phenyl ring 2: C(25), C(26), C(27), C(28), C(29), C(30)			
$0.9794X + 0.1134Y - 0.1669Z = -5.7584$			$\chi^2 = 79$
C(25)	−0.018(3)	C(28)	−0.012(4)
C(26)	0.012(4)	C(29)	−0.001(3)
C(27)	0.006(4)	C(30)	0.013(3)
G. Terminal phenyl ring 1: C(31), C(32), C(33), C(34), C(35), C(36)			
$-0.5495X - 0.8199Y - 0.1604Z = 4.4359$			$\chi^2 = 7$
C(31)	−0.004(3)	C(34)	−0.002(4)
C(32)	0.006(4)	C(35)	−0.001(4)
C(33)	−0.005(4)	C(36)	0.004(4)
H. Terminal phenyl ring 2: C(37), C(38), C(39), C(40), C(41), C(42)			
$-0.9403X - 0.0058Y - 0.3403Z = 4.3161$			$\chi^2 = 17$
C(37)	−0.007(3)	C(40)	−0.009(4)
C(38)	0.004(3)	C(41)	0.003(4)
C(39)	0.005(4)	C(42)	0.006(4)
I. Terminal phenyl ring 3: C(43), C(44), C(45), C(46), C(47), C(48)			
$-0.4809X - 0.6621Y - 0.5747Z = 0.6670$			$\chi^2 = 3$
C(43)	−0.003(3)	C(46)	−0.002(4)
C(44)	0.002(3)	C(47)	−0.001(4)
C(45)	0.001(4)	C(48)	0.004(4)
J. Terminal phenyl ring:4: C(49), C(50), C(51), C(52), C(53), C(54)			
$-0.0763X - 0.1980Y - 0.9772Z = -5.2008$			$\chi^2 = 5$
C(49)	0.002(3)	C(52)	0.005(4)
C(50)	−0.003(3)	C(53)	−0.007(5)
C(51)	0.001(4)	C(54)	0.002(4)

TABLE 3 (continued)

Dihedral angles between planes

Plane 1	Plane 2	Angle (deg)
A	C	3.2
B	D	2.4
C	D	−62.2
C	E	−33.8
C	F	37.6
C	G	−30.4
C	H	−57.9
D	E	47.8
D	F	−52.3
D	I	24.6
D	J	41.8
E	F	−60.1

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[a] The equation of the plane is of the form $aX + bY + cZ = D$, where X, Y and Z are orthogonalized coordinates.

Experimental section

Proton NMR spectra were recorded on either a Varian A-60 or a Perkin-Elmer R-12A spectrometer, infrared spectra were recorded on a Beckman IR-10 spectrometer, and mass spectra were recorded on a Perkin-Elmer-Hitachi RMU-6L instrument. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Melting points were measured in sealed capillary tubes under nitrogen and are uncorrected. (η^5-C_5H_5)Co(CO)$_2$ [2], (η^5-C_5H_5)Rh(CO)$_2$ [5] and 1,2-bis(phenylethynyl)-benzene [15] (m.p. 51—52°C) [11] were prepared by literature procedures.

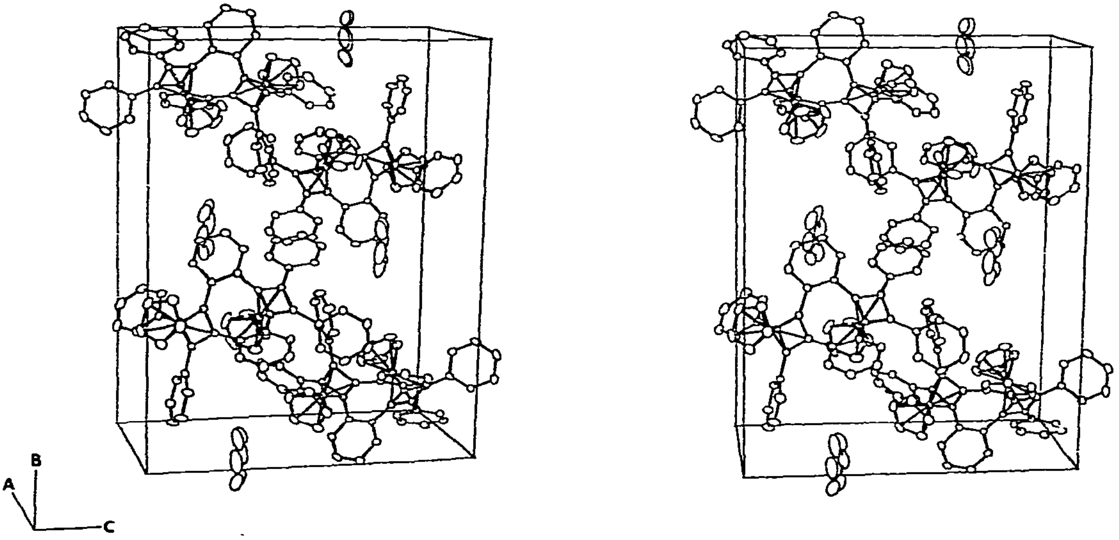

Fig. 2. Stereoscopic view of the unit cell, illustrating the molecular packing of 9b and the location of the benzene solvent molecules.

TABLE 4

IMPORTANT INTRAMOLECULAR CONTACTS (Å)

H(2)....H(42)	2.38
H(3)....H(50)	2.36
H(4)....H(44)	2.54
H(5)....H(32)	2.73
H(6)....H(20)	2.64
H(7)....H(26)	2.75
H(8)....H(26)	2.45
H(9)....H(48)	2.92
H(10)....H(20)	2.93
H(10)....H(54)	2.54
H(20)....H(54)	2.11
H(26)....H(44)	2.91
H(29)....H(32)	2.78
H(36)....H(38)	2.19
H(48)....H(50)	2.68

Reaction of η^5-cyclopentadienyldicarbonylcobalt and 1,2-bis(phenylethynyl)-benzene

1,2-Bis(phenylethynyl)benzene (4) (2.5 g, 9 mmol) and η^5-cyclopentadienyldicarbonylcobalt (1) (1.8 g, 10 mmol) were mixed with 250 ml of xylene in a 500 ml round bottom flask. The reaction vessel was flushed several times with nitrogen and then covered with aluminum foil in order to minimize exposure to light. The reaction mixture was heated at reflux with magnetic stirring for 12 h, allowed to cool to room temperature, concentrated, and placed on a 3.5 × 100 cm alumina column (DAMAG, deactivated with 5% water) which had been packed in heptane.

A yellow band was eluted from the column with 1/9 benzene/heptane and was shown to contain three components by TLC. A minimum amount of silica (Woelm) was added to a methylene chloride solution of this band, and the mixture was then evaporated to dryness and placed on top of a silica column (3.2 × 100 cm) packed dry in nylon tubing. Elution with 1/4 benzene/heptane resulted in three yellow bands which were cut from the column and extracted with methylene chloride.

The yellow band of highest R_f was rechromatographed on an alumina column (3.2 × 48 cm). Elution with 1/4 benzene/heptane and evaporation to dryness yielded 0.62 g (25%) of 1,2,4-triphenyl-3-(*o*-phenylethynyl-phenyl)-biphenylene (7). An analytical sample was prepared by recrystallization from benzene/heptane; light yellow crystals, m.p. 190–191°C.

Anal. Found: C, 94.87; H, 5.20. Calcd for $C_{44}H_{28}$: C, 94.94; H, 5.06%. The molecular weight was 556 as determined by mass spectrometry (calcd 556). The following major bands were observed in the infrared spectrum (KBr): 3080m, 1600m, 1490s, 1440m, 1410m, 1310w, 1220m, 1150s, 1070w, 1028m, 910m, 760(sh), 740s and 690s cm^{-1}. The proton NMR spectrum ($CDCl_3$) consisted of a multiplet in the aromatic region from τ 2.6–3.7.

The yellow band of middle R_f was purified by trituration with benzene followed by recrystallization from benzene/heptane to produce 1.18 g (33%) of yellow crystals of 9, m.p. 394–395°C.

Anal. Found: C, 80.41; H, 4.89; Co, 15.05. Calcd. for $C_{54}H_{38}Co_2$: 80.60; H, 4.76; Co, 14.64%. The molecular weight was 804 as determined by mass spectrometry (calcd 804). The infrared spectrum (KBr) consisted of the following major bands: 3080m, 1600m, 1490m, 1100w, 1000m, 800m, 760s, 740(sh) and 690s cm^{-1}. The proton NMR spectrum ($CDCl_3$) contained a singlet at τ 5.42 (η^5-C_5H_5Co) and a multiplet in the aromatic region from τ 2.17—3.24.

The yellow band of lowest R_f (0.160 g, 5%) was recrystallized from benzene/hexane in the form of yellow microcrystals, m.p. 354—355°C (13).

Anal. Found: C, 88.97; H, 5.08; Co, 6.00. Calcd for $C_{71}H_{47}Co$: C, 88.91; H, 4.94; Co, 6.15%. The molecular weight was 958 as determined by mass spectrometry (calcd 958). The following major bands were present in the infrared spectrum (KBr): 3080m, 1600m, 1490s, 1440m, 1220w, 1150m, 1070w, 1028m, 910m, 760(sh), 740s and 690s cm^{-1}. The proton NMR spectrum ($CDCl_3$) contained two singlets of approximately equal intensities in the η^5-C_5H_5Co region at τ 5.05 and 5.12, a weak singlet at τ 4.95, and a multiplet in the aromatic region from τ 2.3—3.9.

A red band was subsequently eluted from the original column with chloroform to produce 28 mg of crude material. Fractional crystallization from ethyl ether/hexane afforded ca. 5 mg of product (14), which after drying in vacuo at 100°C had a melting range of 238—248°C. The molecular weight was 986 as determined by mass spectrometry (calcd 986). The infrared spectrum (KBr) contained the following major bands: 3060m, 2920s, 1600s, 1590(sh), 1490m, 1440m, 1390w, 1260w, 1080w, 1020w, 810m, 750m, 740(sh), and 690m cm^{-1}. The proton NMR spectrum ($CDCl_3$) contained a series of singlets in the η^5-C_5H_5Co region between τ 4.8—5.1, and a multiplet in the aromatic region from τ 1.2—4.0.

The origin of the original column was extracted with acetone. After evaporation to dryness, the residue was dissolved in a minimum amount of methylene chloride, the solution mixed with a small amount of alumina, dried under vacuum, and the residue placed on top of an alumina column (3.2 × 50 cm) which had been packed dry. After elution with ethyl ether, the red band of lowest R_f was extracted with acetone, recrystallized from methylene chloride/ether and dried to yield ca. 5 mg of product (12), m.p. 225—228°C. The molecular weight was 860 as determined by mass spectrometry (calcd 860). The following major bands were present in the infrared spectrum (KBr): 3030m, 2940w, 1600s, 1590(sh), 1500m, 1440m, 1400w, 1370w, 1250w, 1150w, 1080w, 1030w, 810m, 750m, and 690s cm^{-1}. The proton NMR spectrum ($CDCl_3$) consisted of a η^5-C_5H_5Co peak at τ 1.2—4.0.

Reaction of η^5-cyclopentadienyldicarbonylrhodium and 1,2-bis(phenylethynyl)benzene

1,2-Bis(phenylethynyl)benzene (4) (2.3 g, 8.23 mmol) and η^5-cyclopentadienyldicarbonylrhodium (2) (1.85 g, 8.26 mmol) were mixed with 25 ml of xylene in a 50 ml round bottom flask with nitrogen sidearm. The reaction vessel was flushed several times with nitrogen and then covered with aluminum foil in order to minimize exposure to the light. The reaction mixture was heated at reflux for 24 h, allowed to cool to room temperature, filtered, and chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with hexane produced a small red band which was shown by TLC to contain small amounts of the starting rhodium complex (2). Continued elution with 1/1 benzene/hexane removed a yellow band which was rechromatographed on a dry alumina column (2.0 × 15 cm), and the product was recrystallized from benzene/hexane to produce 100 mg (4%) of 1,2,4-triphenyl-3-(*o*-phenylethynyl-phenyl)biphenylene (7), m.p. 190—191°C.

Elution of the original column with benzene removed a green band which was chromatographed on a dry alumina column (2.0 × 20 cm). A blue-green band was initially eluted with benzene and this was evaporated to dryness to yield 70 mg (2%) of a dark-green solid (15), m.p. 178—180°C.

Anal. Found: C, 67.01; H, 4.33. Calcd for $C_{59}H_{43}Rh_3$: C, 66.81; H, 4.09%. The molecular weight was 1060 as determined by mass spectrometry (calcd 1060). The following major bands were observed in the infrared spectrum (KBr): 1600s, 1490—1400m, 1260w, 1150w, 1065w, 1000w, 910w, 790—740s, 690s. The proton NMR spectrum ($CDCl_3$) consisted of three η^5-C_5H_5Rh peaks at τ 5.13, 5.27 and 5.40, and a multiplet in the aromatic region from τ 2.6—3.4.

Further elution of the dry alumina column produced a large blue band which was evaporated to dryness and recrystallized from benzene/hexane to yield 280 mg of dark blue crystals, m.p. 115—120°C (dec.); (Found: C, 67.62; H, 3.49%). The compound appeared to detonate in the probe of the mass spectrometer and a spectrum could not be obtained. The following major bands were observed in the infrared spectrum (KBr): 1800m, 1680s, 1475w, 1440w, 1410w, 1150w, 1000m, 780s, 740s, and 690s cm^{-1}. The proton NMR spectrum ($CDCl_3$) consisted of a sharp singlet at τ 5.05 in the η^5-C_5H_5Rh region and multiplet absorptions in the aromatic region from τ 2.6—3.5.

Continued elution of the original column with 1/3 ethyl ether/hexane removed a black band. This band was evaporated to dryness and recrystallized from benzene/hexane to yield 60 mg (4%) of a black solid identified as tris(μ-carbonyl)-tris-(η^5-cyclopentadienylrhoduim) (16), m.p. 265—270°C (dec.). A molecular ion was observed at *m/e* 728, corresponding to the thermal decomposition product $(C_5H_5Rh)_4(CO)_2$ [14]. The proton NMR spectrum ($CDCl_3$) consisted of a singlet at τ 4.57 (η^5-C_5H_5Rh).

A final yellow-brown band was removed from the original column by elution with ethyl ether. This band was rechromatographed in benzene on an alumina column (2 × 15 cm) which had been packed dry. The major yellow band was removed and recrystallized from benzene/hexane to yield 100 mg (3%) of a yellow solid identified as the mixed complex (17), m.p. 238—240°C (dec.).

Anal. Found: C, 71.96; H, 4.31. Calcd for $C_{55}H_{38}ORh_2$: C, 71.75; H, 4.16%. The molecular weight was 920 as determined by mass spectrometry (calcd 920). The following major bands were observed in the infrared spectrum (KBr): 1600s, 1590(sh), 1490s, 1440m, 1030w, 1000w, 800m, 740m and 690m cm^{-1}. The proton NMR spectrum ($CDCl_3$) consisted of two peaks of equal intensity at τ 4.72 and 5.35 in the η^5-C_5H_5Rh region, and a multiplet in the aromatic region from τ 2.6—3.7.

X-ray data collection and structure determination

Crystals suitable for X-ray studies were grown from benzene/hexane mixtures. The crystal used was nearly a rectangular parallelepiped of dimensions 0.25 × 0.19 × 0.22 mm. The unit cell dimensions and an orientation matrix for data collection were determined by least-squares refinement of 25 accurately-centered high angle reflections on an Enraf-Nonius CAD-4 diffractometer. The unit cell is monoclinic with dimensions $a = 10.652(5)$, $b = 23.690(6)$, $c = 17.204(4)$ Å, $\beta = 90.21(3)^\circ$; $V = 4341(4)$ Å^3. The choice of $P2_1/n$ as the space group was confirmed by the systematic absences of $h0l$ with $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$. Assuming $Z = 4$, a density value of 1.351(1) g/cm^3 was calculated, including one benzene solvent for every molecule of **9b**.

Intensity data were collected by the θ—2θ scan technique out to a value of $2\theta_{\max} = 50^\circ$ with monochromatized (graphite crystal) Mo—$K\alpha$ radiation ($\lambda = 0.71073$ Å) at a 4.0° takeoff 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 per reflection was also variable and amounted to $3 \times (0.7 + 0.347 \tan \theta_{\lambda\alpha_2})$ *. Right and left backgrounds were each scanned for 25% of the time required for the total peak scan. Three standard reflections were monitored for intensity every 100 reflections and orientation controls about every 400 reflections. The intensities of these standards fluctuated randomly with a deviation of less than ±2% about the mean.

A total of 8286 reflections were scanned in the hkl and $hk\bar{l}$ octants, of which 5509 were found to have intensities greater than or equal to 3σ, where $\sigma = [\text{total counts} + \text{background counts} + (pI)^2]^{1/2}$, and therefore were considered to be observed. Here $p = 0.05$. Another 317 non-unique reflections ($0kl$, $l > 0$) were rejected yielding 5192 reflections for the least squares refinement. The intensities were corrected for Lorentz and double polarization effects [21]. An absorption correction, with mass absorption coefficient 8.357 cm^{-1}, was calculated and applied based upon the measured crystal dimensions.

Trial positions for the cobalt atoms were obtained from a three dimensional Patterson map which gave an immediate R factor of 0.41. Subsequent difference Fourier maps revealed the locations of the carbon atoms in **9b**, and after several cycles of isotropic full-matrix least-squares refinement, R was reduced to 0.136. The R factor was further reduced to 0.076 following several cycles of full-matrix refinement with anisotropic temperature factors for all non-hydrogen atoms in **9b**, at which point a difference Fourier revealed the presence of several peaks with electron densities on the order of 1.8 e/Å^3. Their high thermal parameters, location between molecules of **9b**, and shape indicated a benzene solvent molecule in a general position. Block-matrix refinement (at first isotropic; then anisotropic) of the solvent carbon parameters, holding the parameters of **9b** fixed, led to an R of 0.062. Hydrogen atoms were next placed in their calculated positions (C—H) = 0.95 Å) on both the **9b** and solvent molecules and included as a fixed contribution. Each hydrogen atom was assigned the isotropic temperature factor of the carbon atom to which it is bonded. Full-matrix refinement on the non-hydrogen atoms for two more cycles yielded shifts in the parameters which were less than 1.0 of their standard deviations

(continued on p. 264)

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* The angular scan width is $A + 0.347 \tan(\theta_{\lambda\alpha_2})$, where $\theta_{\lambda\alpha_2}$ is determined from the formula

$$\theta_{\lambda\alpha_2} = \theta_{\lambda\alpha_1} + \left(\frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha}\right)\left(\frac{360}{2\pi}\right)\tan(\theta_{\lambda\alpha_1})$$

and A depends on the mosaic spread and on the divergence of the primary beam.

TABLE 5

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS [a] AND THEIR ESTIMATED STANDARD DEVIATIONS [b] FOR NONHYDROGEN ATOMS

Atom	X	Y	Z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Co(1)	0,57847(4)	0,14974(2)	−0,16042(2)	0,00484(3)	0,00123(1)	0,00196(1)	−0,00090(3)	−0,00037(4)	0,00017(2)
Co(2)	0.30059(4)	0,13105(2)	−0,42844(2)	0,00616(4)	0,00134(1)	0,00192(1)	−0.00037(3)	−0,00144(4)	0,00011(2)
C(1)	0,7188(4)	0,2026(2)	−0,1249(2)	0.0117(4)	0,00289(9)	0,00331(15)	−0.0073(3)	−0,0037(4)	0,0007(2)
C(2)	0,6325(4)	0,2330(2)	−0,1648(3)	0,0112(4)	0,00146(8)	0,00714(22)	−0,0027(3)	0,0037(5)	0,0002(2)
C(3)	0,6245(4)	0,2118(2)	−0,2376(2)	0.0148(4)	0,00406(10)	0,00450(15)	−0,0109(3)	−0,0069(5)	0,0056(2)
C(4)	0,7068(4)	0,1672(2)	−0,2439(3)	0,0195(5)	0,00424(11)	0,00518(17)	−0,0133(3)	0,0139(5)	−0,0052(2)
C(5)	0,7667(4)	0,1619(2)	−0,1720(4)	0.0047(3)	0,00218(10)	0,01208(33)	−0,0013(3)	0,0037(6)	0,0022(3)
C(6)	0,1116(4)	0,1156(2)	−0.4451(2)	0.0069(3)	0.00290(10)	0,00407(15)	−0,0019(3)	−0,0031(4)	−0,0013(2)
C(7)	0,1788(4)	0,0667(2)	−0.4610(2)	0.0110(4)	0,00186(8)	0,00396(15)	−0.0027(3)	−0.0046(4)	−0,0005(2)
C(8)	0,2626(4)	0,0790(2)	−0,5215(2)	0.0107(4)	0,00259(9)	0,00288(13)	0.0009(3)	−0,0041(4)	−0,0023(3)
C(9)	0,2459(4)	0,1364(2)	−0,5427(2)	0.0120(4)	0.00321(11)	0,00220(12)	−0,0019(4)	−0,0038(4)	0,0010(2)
C(10)	0,1515(4)	0,1590(2)	−0.4952(2)	0,0100(4)	0,00229(9)	0,00374(14)	0,0011(3)	−0,0061(4)	0,0004(2)
C(11)	0,4618(3)	0,1252(1)	−0,0769(2)	0.0046(3)	0,00113(6)	0,00182(9)	−0,0007(2)	−0,0000(3)	0,0001(1)
C(12)	0,5428(3)	0,0789(1)	−0.1018(2)	0.0051(3)	0,00108(6)	0,00181(10)	−0,0003(2)	0,0001(3)	0,0001(1)
C(13)	0,4815(3)	0,0797(1)	−0.1789(2)	0.0046(3)	0,00116(6)	0,00180(10)	−0,0005(2)	−0,0003(3)	0,0002(1)
C(14)	0.4004(3)	0.1260(1)	−0.1535(2)	0.0048(3)	0.00099(5)	0,00182(10)	−0,0006(2)	0.0001(3)	0,0003(1)
C(15)	0,3992(3)	0,1928(1)	−0.3824(2)	0.0053(3)	0,00112(6)	0,00185(10)	0,0002(2)	−0,0003(3)	0,0001(1)
C(16)	0.4800(3)	0,1457(1)	−0.4058(2)	0.0057(3)	0,00125(6)	0,00180(10)	−0,0003(2)	−0,0005(3)	−0,0000(1)
C(17)	0.4239(3)	0.1100(1)	−0.3452(2)	0.0058(3)	0,00103(5)	0,00167(9)	−0,0002(2)	−0,0008(3)	0,0000(1)
C(18)	0,3437(3)	0.1568(1)	−0.3214(2)	0.0050(3)	0,00110(6)	0,00209(10)	−0,0003(2)	−0,0010(3)	0,0000(1)
C(19)	0,2559(3)	0.1676(1)	−0.2573(2)	0.0048(3)	0.00103(6)	0,00229(10)	−0,0007(2)	−0,0003(3)	−0,0000(1)
C(20)	0.1428(3)	0.1945(1)	−0.2725(2)	0.0060(3)	0.00166(7)	0,00259(12)	0,0007(2)	−0,0010(3)	0,0007(2)
C(21)	0,0569(3)	0.2070(2)	−0.2149(2)	0.0049(3)	0.00216(8)	0,00344(14)	0,0016(3)	−0,0003(3)	0,0002(2)
C(22)	0,0823(3)	0,1910(2)	−0.1396(2)	0.0050(3)	0.00207(8)	0,00308(13)	0,0009(3)	0,0013(3)	−0,0006(2)
C(23)	0.1940(3)	0.1645(1)	−0.1226(2)	0.0052(3)	0.00171(7)	0,00210(11)	−0,0005(2)	0,0001(3)	−0,0003(1)
C(24)	0.2833(3)	0.1530(1)	−0.1794(2)	0.0043(2)	0,00114(6)	0,00219(10)	−0.0005(2)	−0,0004(3)	0,0000(1)
C(25)	0.4471(3)	0,0517(1)	−0.3194(2)	0.0059(3)	0,00112(6)	0,00201(10)	−0.0000(2)	−0,0002(3)	0,0001(1)
C(26)	0,4457(3)	0,0081(1)	−0,3746(2)	0.0094(4)	0,00141(7)	0,00201(11)	0.0006(3)	−0,0011(3)	−0,0004(1)
C(27)	0.4651(4)	−0.0472(1)	−0.3543(2)	0.0117(4)	0.00119(6)	0,00309(13)	0.0005(3)	−0,0015(4)	−0,0012(2)
C(28)	0.4885(4)	−0.0607(1)	−0.2771(2)	0.0112(4)	0.00094(6)	0.00351(13)	0.0006(3)	−0,0012(4)	0.0000(2)
C(29)	0.4942(3)	−0.0188(1)	−0.2225(2)	0.0081(3)	0,00116(6)	0.00248(11)	0.0004(2)	−0,0011(3)	0.0004(1)

C(30)	0,4755(3)	0,0379(1)	−0,2417(2)	0,0048(3)	0,00100(5)	0,00205(10)	−0,0000(2)	−0,0000(3)	−0,0000(1)
C(31)	0,6421(3)	0,0445(1)	−0,0671(2)	0,0047(3)	0,00119(6)	0,00215(10)	−0,0001(2)	−0,0007(3)	0,0001(1)
C(32)	0,7378(3)	0,0215(1)	−0,1126(2)	0,0068(3)	0,00167(7)	0,00259(12)	0,0006(3)	0,0004(3)	0,0005(2)
C(33)	0,8320(3)	−0,0109(2)	−0,0802(2)	0,0068(3)	0,00163(7)	0,00382(15)	0,0013(3)	0,0011(4)	−0,0001(2)
C(34)	0,8326(3)	−0,0223(1)	−0,0017(2)	0,0062(3)	0,00144(7)	0,00414(15)	0,0007(2)	−0,0026(4)	0,0002(2)
C(35)	0,7394(3)	−0,0007(1)	0,0439(2)	0,0078(3)	0,00137(6)	0,00267(12)	−0,0004(3)	−0,0023(3)	0,0010(1)
C(36)	0,6449(3)	0,0323(1)	0,0122(2)	0,0061(3)	0,00127(6)	0,00230(11)	−0,0005(2)	−0,0007(3)	−0,0001(1)
C(37)	0,4312(3)	0,1543(1)	−0,0029(2)	0,0044(2)	0,00121(6)	0,00205(10)	0,0004(2)	−0,0009(3)	−0,0002(1)
C(38)	0,3937(3)	0,1225(1)	0,0608(2)	0,0065(3)	0,00142(6)	0,00227(11)	0,0008(2)	−0,0000(3)	0,0001(1)
C(39)	0,3541(4)	0,1490(2)	0,1284(2)	0,0084(3)	0,00235(8)	0,00225(12)	0,0020(3)	0,0002(4)	0,0002(2)
C(40)	0,3519(4)	0,2069(2)	0,1333(2)	0,0082(4)	0,00264(9)	0,00272(13)	0,0019(3)	−0,0006(4)	−0,0021(2)
C(41)	0,3867(4)	0,2386(2)	0,0701(2)	0,0098(4)	0,00145(7)	0,00466(16)	0,0006(3)	0,0002(4)	−0,0020(2)
C(42)	0,4260(3)	0,2125(1)	0,0025(2)	0,0082(3)	0,00138(7)	0,00316(13)	−0,0004(3)	0,0014(4)	−0,0003(2)
C(43)	0,5874(3)	0,1388(1)	−0,4581(2)	0,0064(3)	0,00137(7)	0,00207(10)	−0,0004(2)	0,0002(3)	−0,0006(1)
C(44)	0,6793(3)	0,0985(2)	−0,4423(2)	0,0071(3)	0,00147(7)	0,00315(13)	0,0000(3)	0,0000(3)	−0,0005(2)
C(45)	0,7842(3)	0,0938(2)	−0,4892(2)	0,0067(3)	0,00234(9)	0,00484(16)	0,0002(3)	0,0008(4)	−0,0020(2)
C(46)	0,7984(4)	0,1290(2)	−0,5524(2)	0,0089(4)	0,00288(10)	0,00444(16)	−0,0023(3)	0,0055(4)	−0,0028(2)
C(47)	0,7089(4)	0,1686(2)	−0,5689(2)	0,0130(4)	0,00240(9)	0,00311(13)	−0,0022(3)	0,0053(4)	−0,0008(2)
C(48)	0,6028(4)	0,1739(2)	−0,5227(2)	0,0094(4)	0,00173(7)	0,00241(12)	−0,0008(3)	0,0013(4)	−0,0001(2)
C(49)	0,3984(3)	0,2534(1)	−0,3995(2)	0,0071(3)	0,00111(6)	0,00182(10)	−0,0004(2)	−0,0009(3)	0,0002(1)
C(50)	0,5127(3)	0,2814(1)	−0,4126(2)	0,0063(3)	0,00136(6)	0,00277(12)	0,0001(2)	0,0003(3)	0,0002(1)
C(51)	0,5151(4)	0,3380(2)	−0,4287(2)	0,0092(4)	0,00131(7)	0,00362(14)	−0,0013(3)	0,0013(4)	0,0002(2)
C(52)	0,4056(4)	0,3687(2)	−0,4322(3)	0,0126(5)	0,00108(7)	0,00510(18)	0,0000(3)	−0,0002(5)	0,0011(2)
C(53)	0,2941(4)	0,3426(2)	−0,4189(3)	0,0094(4)	0,00142(7)	0,00620(20)	0,0022(3)	−0,0013(5)	0,0013(2)
C(54)	0,2900(3)	0,2856(2)	0,4033(2)	0,0066(3)	0,00160(7)	0,00471(16)	−0,0004(3)	−0,0006(4)	0,0012(2)
CX(1)	0,5652(8)	0,4279(4)	0,7877(4)	0,0319(12)	0,00761(27)	0,00648(28)	0,0069(10)	0,0011(10)	0,0065(4)
CX(2)	0,4525(8)	0,4229(4)	0,7646(4)	0,0344(12)	0,01010(34)	0,00488(24)	−0,0174(10)	−0,0031(9)	0,0039(5)
CX(3)	0,3823(6)	0,4657(5)	0,7522(4)	0,0134(7)	0,01434(45)	0,00568(27)	0,0056(9)	−0,0005(8)	0,0046(6)
CX(4)	0,4237(8)	0,5205(4)	0,7600(4)	0,0360(11)	0,00849(25)	0,00699(32)	0,0203(7)	0,0080(10)	−0,0011(5)
CX(5)	0,5487(8)	0,5253(3)	0,7869(4)	0,0391(13)	0,00584(23)	0,00534(27)	−0,0035(9)	0,0105(9)	−0,0026(4)
CX(6)	0,6168(6)	0,4771(4)	0.7990(3)	0,0161(7)	0,01041(36)	0,00489(24)	−0,0027(9)	−0,0021(7)	0,0033(5)

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[a] The form of the anisotropic thermal ellipsoid parameter is $\exp[-(B_{1,1}h^2 + B_{2,2}k^2 + B_{3,3}l^2 + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$. [b] Numbers in parentheses are the e.s.d.'s in the least significant digits in this and succeeding tables.

(less than 3.5σ for the solvent atoms); therefore, the refinement was considered to be complete.

The final value of the residual, $R(\mathrm{F}) = \dfrac{\Sigma||Fo| - |Fc||}{\Sigma|Fo|}$, was 0.037, and the value of the weighted residual, $R_{\mathrm{w}}(\mathrm{F}) = \left[\dfrac{\Sigma w(|Fo| - |Fc|)^2}{\Sigma w|Fo|^2}\right]^{1/2}$, was 0.050. The function minimized in the refinement was $\Sigma w(|Fo| - |Fc|)^2$, with weights, w, assigned by the expression $w = 1/\sigma_{Fo}^2$ and $\sigma_{Fo}^2 = [\sigma_I^2 + (pI)^2]^{1/2}/LP$. The final e.s.d. of an

TABLE 6

POSITIONAL AND THERMAL PARAMETERS FOR HYDROGEN ATOMS

Atom	*X*	*Y*	*Z*	B (iso)
H(1)	0.7437(0)	0.2087(0)	−0.0689(0)	5.5500(0)
H(2)	0.5851(0)	0.2651(0)	−0.1449(0)	6.3900(0)
H(3)	0.5720(0)	0.2241(0)	−0.2811(0)	6.4900(0)
H(4)	0.7273(0)	0.1419(0)	−0.2883(0)	6.5100(0)
H(5)	0.8307(0)	0.1348(0)	−0.1578(0)	7.0600(0)
H(6)	0.0432(0)	0.1179(0)	−0.4074(0)	5.2700(0)
H(7)	0.1737(0)	0.0298(0)	−0.4361(0)	5.3100(0)
H(8)	0.3215(0)	0.0530(0)	−0.5447(0)	4.6100(0)
H(9)	0.2942(0)	0.1554(0)	−0.5816(0)	5.1700(0)
H(10)	0.1204(0)	0.1968(0)	−0.4958(0)	5.2400(0)
H(20)	0.1221(0)	0.2054(0)	−0.3260(0)	3.4000(0)
H(21)	−0.0212(0)	0.2271(0)	−0.2260(0)	4.3600(0)
H(22)	0.0231(0)	0.1979(0)	−0.0988(0)	3.9000(0)
H(23)	0.2102(0)	0.1518(0)	−0.0705(0)	3.3300(0)
H(26)	0.4301(0)	0.0185(0)	−0.4286(0)	3.5900(0)
H(27)	0.4657(0)	−0.0759(0)	−0.3951(0)	4.1600(0)
H(28)	0.5043(0)	−0.0994(0)	−0.2620(0)	4.3500(0)
H(29)	0.5078(0)	−0.0279(0)	−0.1678(0)	3.3300(0)
H(32)	0.7373(0)	0.0277(0)	−0.1687(0)	3.9800(0)
H(33)	0.8955(0)	−0.0261(0)	−0.1146(0)	4.1800(0)
H(34)	0.8991(0)	−0.0441(0)	0.0202(0)	4.2300(0)
H(35)	0.7345(0)	−0.0104(0)	0.0977(0)	3.6600(0)
H(36)	0.5805(0)	0.0468(0)	0.0457(0)	3.2000(0)
H(38)	0.3925(0)	0.0827(0)	0.0580(0)	3.3500(0)
H(39)	0.3331(0)	0.1272(0)	0.1720(0)	4.4500(0)
H(40)	0.3268(0)	0.2248(0)	0.1809(0)	4.7600(0)
H(41)	0.3766(0)	0.2790(0)	0.0731(0)	4.7800(0)
H(42)	0.4528(0)	0.2351(0)	−0.0418(0)	4.0100(0)
H(44)	0.6687(0)	0.0743(0)	−0.3971(0)	4.0800(0)
H(45)	0.8480(0)	0.0639(0)	−0.4761(0)	4.9600(0)
H(46)	0.8710(0)	0.1220(0)	−0.5835(0)	5.8100(0)
H(47)	0.7271(0)	0.1934(0)	−0.6090(0)	5.7800(0)
H(48)	0.5380(0)	0.2013(0)	−0.5371(0)	3.9800(0)
H(50)	0.5890(0)	0.2609(0)	−0.4081(0)	3.4700(0)
H(51)	0.5947(0)	0.3556(0)	−0.4393(0)	4.6100(0)
H(52)	0.4105(0)	0.4089(0)	−0.4419(0)	5.0800(0)
H(53)	0.2157(0)	0.3647(0)	−0.4170(0)	5.0200(0)
H(54)	0.2096(0)	0.2662(0)	−0.3976(0)	4.3500(0)
HX(1)	0.6144(0)	0.3945(0)	0.7984(0)	11.9000(0)
HX(2)	0.4161(0)	0.3826(0)	0.7546(0)	13.4000(0)
HX(3)	0.2954(0)	0.4614(0)	0.7377(0)	11.1000(0)
HX(4)	0.3708(0)	0.5527(0)	0.7480(0)	11.9000(0)
HX(5)	0.5851(0)	0.5660(0)	0.7971(0)	11.7000(0)
HX(6)	0.7030(0)	0.4819(0)	0.8154(0)	11.1000(0)

observation of unit weight was 1.41. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber [22], corrected for anomalous dispersion (both real and imaginary parts). Scattering factors for hydrogen atoms were taken from Stewart, et al. [23]. The final difference Fourier was featureless, with a number of peaks of height less than ±0.2 $e/Å^3$ distributed randomly throughout the map. Table 5 contains the positional and anisotropic temperature factors. Solvent atoms have an X in their label. Positional and isotropic temperature factors for the hydrogen atoms are given in Table 6. A listing of structure factors is available as supplementary material *.

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