

REACTION OF A DIPHENYLACETYLENE—COBALT COMPLEX WITH ALKYL DIAZOACETATES

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Summary

The diphenylacetylene—cobalt complex, $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})$ (I) reacted with alkyl diazoacetates (II, alkyl = methyl, ethyl, and t-butyl) at room temperature to give two isomers of the mononuclear cobalt complex, $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PhC}_2\text{Ph})(\text{CHCO}_2\text{R})_2$ (III and IV) and two isomers of the dinuclear cobalt complex $[\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PhC}_2\text{Ph})(\text{CHCO}_2\text{R})]_2$ (V and VI).

The complexes III and IV are diene complexes, *syn,syn*- and *syn,anti*- (dialkyl 2,3-diphenylmuconate)- η^5 -cyclopentadienylcobalt, respectively. The structure of Vb (R = C₂H₅) was determined by X-ray diffraction as $\mu\text{-}[1\text{-}3\text{-}\eta^3 : 1,4,5\text{-}\eta^3\text{-}1,6\text{-bis(ethoxycarbonyl)-}2,3,4,5\text{-tetraphenylhexa-}2,4\text{-diene-}1,1\text{-diyl}]$ bis(η^5 -cyclopentadienylcobalt)(Co—Co). The complex VI is the bis(η^3 -allyl)cobalt complex, $\mu\text{-}[1\text{-}3\text{-}\eta^3 : 4\text{-}6\text{-}\eta^3\text{-}1,6\text{-anti,anti-bis(alkoxycarbonyl)-}2,3,4,5\text{-tetraphenylhexa-}1,3,5\text{-triene}]$ bis(η^5 -cyclopentadienylcobalt)(Co—Co) according to its ¹H NMR spectrum.

The formation of these products was rationalized in terms of a cobaltacyclobutene intermediate.

Introduction

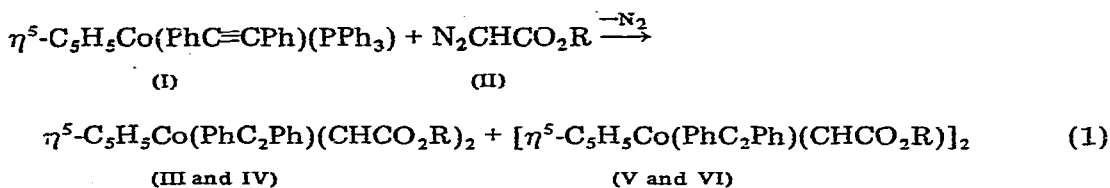
In recent years, the interactions of carbenes with transition metal complexes have been drawing much attention [1]. Previously we have reported that the stepwise addition of isocyanides to an acetylene—cobalt complex, $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})$ (I) leads to the formation of metallacycles such as 3-iminocobaltacyclobut-2-ene and 2,5-diiminocobaltacyclopent-3-ene derivatives [2]. In view of the electronic analogy between a carbene and an isocyanide, we were interested in the interaction of a carbene with I. If the reaction of a carbene with I is similar to that of an isocyanide, the formation of cobaltacyclobut-2-ene and cobaltacyclopent-3-ene derivatives may be expected.

We describe here the reaction of I with alkyl diazoacetates, which are potential

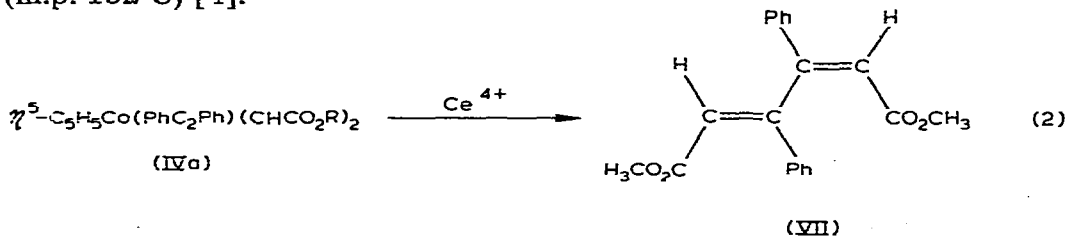
carbene precursors*, and show that the addition of alkoxy-carbonylcarbenes to I occurs analogously to that of isocyanides.

Results and discussion

When the diphenylacetylene-cobalt complex (I) was treated with alkyl diazoacetates (II, alkyl = CH₃, C₂H₅, and t-C₄H₉), in benzene at room temperature, nitrogen has evolved smoothly, and a brownish red solution was obtained. The resolution of the reaction mixture by column chromatography (silica) gave four air-stable complexes, III, IV, V, and VI. The complexes III and IV, which isolated as red crystals, were shown to be mononuclear cobalt complexes of empirical formula $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PhC}_2\text{Ph})(\text{CHCO}_2\text{R})_2$ by elementary analysis and mass spectrometry (Table 1). On the other hand, V and VI, which isolated as dark brown crystals, were shown to be binuclear cobalt complexes of empirical formula $[\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PhC}_2\text{Ph})(\text{CHCO}_2\text{R})]_2$. As shown in Table 2, their yields depended on the molar ratio of II to I. As this ratio increased, the total yields of V and VI decreased, while those of III and IV increased. Further reaction of V and VI with II did not give III and IV, which suggests that the former two are not the precursors for the latter two.



The spectroscopic data for mononuclear cobalt complexes III and IV are shown in Table 3. The ¹H NMR spectra showed that the two alkoxy-carbonyl-methylene units in III are equivalent, and that those in IV are nonequivalent, thus suggesting symmetrical and nonsymmetrical structures, respectively. The appearance of all the methine protons as singlets in these complexes suggests that the alkoxy-carbonylmethylene units are not vicinal and that they are located on opposite sides of the original acetylene unit. This may indicate that a dialkyl 2,3-diphenylmuconate coordinates to the cobalt atom as a diene ligand. As was expected, the decomposition of IVa with ceric ammonium nitrate gave dimethyl *trans,cis*-2,3-diphenylmuconate (VII, m.p. 90–91°C, 75%), the structure of which was deduced by comparison of its melting point and its ¹H NMR spectrum with those of the known *cis,cis* (m.p. 114°C) and *trans,trans* isomers (m.p. 152°C) [4].



* It is known that diazoalkanes react with some transition metal complexes to give carbene complexes [3].

TABLE 1
PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	R	Color	M.p. (°C)	M ⁺ m/e (Found (calcd.))	Found (calcd.) (%)	
					C	H
IIIa	CH ₃	red	182—184	446 (446)	67.74 (67.27)	4.90 (5.19)
IIIb	C ₂ H ₅	red	120—122	474 (474)	68.80 (68.35)	6.07 (5.74)
IIIc	t-C ₄ H ₉	red	190—192	530 (530)	69.57 (70.18)	6.45 (6.65)
IVa	CH ₃	red	162—163	446 (446)	67.55 (67.27)	5.16 (5.19)
IVb	C ₂ H ₅	red	122—123	474 (474)	68.58 (68.35)	5.67 (5.74)
IVc	t-C ₄ H ₉	red	67—69	530 (530)	69.80 (70.18)	6.46 (6.65)
Va	CH ₃	dark brown	208—210	748 (748)	70.60 (70.59)	5.04 (5.12)
Vb	C ₂ H ₅	dark brown	183—185	776 (776)	71.22 (71.13)	5.27 (5.45)
Vc · C ₆ H ₆	t-C ₄ H ₉	dark brown	143—145	832 (832)	73.82 (73.84)	6.16 (6.20)
VIa	CH ₃	dark brown	164—166	748 (748)	70.24 (70.59)	5.22 (5.12)
VIb	C ₂ H ₅	dark brown	168—170	776 (776)	^a	
VIc	t-C ₄ H ₉	dark brown	165—167	832 (832)	^a	

^a Not analyzed.

It is known that in the ¹H NMR spectra of diene complexes the signals of *anti* protons on the terminal carbon atom appear at higher field than those of *syn* protons [5]. Therefore, the singlet due to the methine protons in the NMR spectrum of III which appeared in the δ 0.44—0.64 ppm range could be assigned to the *anti* protons. However, the two singlets in the spectrum of IV which appeared in the δ 1.51—1.70 and 3.67—3.70 ppm ranges could be assigned to the

TABLE 2
DEPENDENCE OF THE PRODUCT YIELDS ON THE II/I REACTANT RATIO

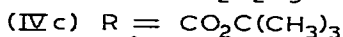
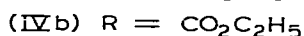
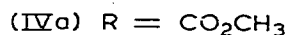
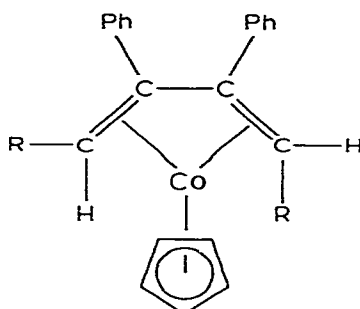
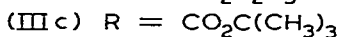
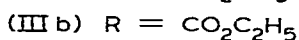
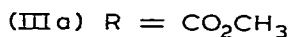
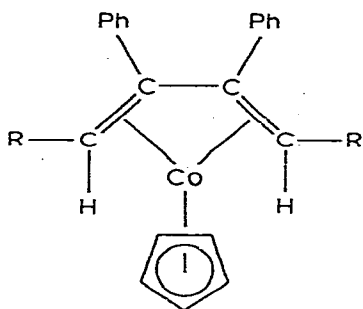
II	II/I	Yield (%)			
		III	IV	V	VI
N ₂ CHCO ₂ CH ₃	1.5	3	7	42	1.5
N ₂ CHCO ₂ CH ₃	3	2	18	32	—
N ₂ CHCO ₂ C ₂ H ₅	1	—	8	38	—
N ₂ CHCO ₂ C ₂ H ₅	2.2	10	17	46	—
N ₂ CHCO ₂ C ₂ H ₅	3	11	22	28	—
N ₂ CHCO ₂ C ₂ H ₅	4	10	24	27	—
N ₂ CHCO ₂ C ₂ H ₅	10	12	36	9	—
N ₂ CHCO ₂ -t-C ₄ H ₉	1.5	—	—	20	2.5
N ₂ CHCO ₂ -t-C ₄ H ₉	5	4	8	12	—

TABLE 3
IR AND NMR SPECTRA OF III AND IV

Compound	IR $\nu(\text{CO})$ (cm^{-1}) ^a	NMR: δ ^b (multiplicity ^c , relative intensity, assignment) (ppm)				
		C_5H_5	R	CH_{anti}	CH_{syn}	Ph
IIIa	1710	5.06(s)	3.53(s, 9, CH_3)	0.60(s, 2)		7.0-7.4(m, 10)
IIIb	1714	5.06(s)	1.11(t ^d , 6, CH_3) 3.96(m ^d , 4, CH_2)	0.59(s, 2)		7.0-7.4(m, 10)
IIIc	1674	5.08(s)	1.25(s, 18, $(\text{CH}_3)_3\text{C}$)	0.44(s, 2)		7.0-7.4(m, 10)
IVa	1705, 1690	5.05(s)	3.53(s, 3, CH_3) 3.59(s, 3, CH_3)	1.70(s, 1)	3.67(s, 1)	7.0-7.4(m, 10)
IVb	1715, 1683	5.07(s)	1.10(t ^e , 3, CH_3), 1.27(t ^e , 3, CH_3) 3.96(q ^e , 2, CH_2), 4.06(q ^e , 2, CH_2)	1.70(s, 1)	3.70(s, 1)	7.0-7.4(m, 10)
IVc	1686, 1675	5.05(s)	1.24(s, 9, $(\text{CH}_3)_3\text{C}$) 1.47(s, 9, $(\text{CH}_3)_3\text{C}$)	1.51(s, 1)	3.08(s, 1)	7.0-7.4(m, 10)

^a KBr pellet. ^b In CDCl_3 . ^c s, singlet; t, triplet; q, quartet; m, multiplet; ^d ABX_3 ($J_{\text{AB}} = 13$ Hz, $J_{\text{AX}} = J_{\text{BX}} = 7$ Hz). ^e $J = 7$ Hz.

anti and *syn* protons, respectively. On the basis of these results, we propose structures III and IV for the *syn,syn* and the *syn,anti* isomers.



The ¹H NMR spectra of IIIa–IIIc also reveal only one resonance due to the equivalent alkoxy-carbonyl groups (IIIa, δ 3.53(s); IIIb, 3.96(m), 1.11(t); IIIc, δ 1.25 ppm (s)), whereas the spectra of IVa–IVc show resonances due to nonequivalent groups (IVa, δ 3.59(s) and 3.53(s); IVb, 4.06(q), 3.96(q), 1.27(t), and 1.10 (t); IVc, 1.47(s) and 1.24 ppm (s)). Both the alkoxy-carbonyl groups in III are in a *cis* relationship with the neighbouring phenyl groups. On the other hand, in IV one alkoxy-carbonyl group is *cis* and the other is *trans* to the respective phenyl group. It should be noted that the lower-field resonance of IV may be assigned to *trans*-alkoxy-carbonyl groups, because the chemical shifts of the signals at higher field are in good agreement with those of III.

The spectroscopic data of binuclear cobalt complexes Va–Vc and VIa–VIc are shown in Table 4. The ¹H NMR spectra of VIa–VIc show the presence of only one kind of η⁵-cyclopentadienyl, alkoxy-carbonyl, and methine group, indicating a symmetrical structure. The spectra of Va–Vc are more complex than those of VIa–VIc. They have two sets of signals of equal intensities corresponding to the presence of nonequivalent η⁵-cyclopentadienyl and alkoxy-carbonyl groups. The most characteristic feature of the spectra is the appearance of two doublets coupled with *J*(HH) 18 Hz, indicating the presence of a methylene group. On the basis of these available spectroscopic data, no single, unambiguous structure could be assigned to the complexes Va–Vc. Accordingly, Vb (R = C₂H₅) was subjected to a single crystal X-ray diffraction study.

A stereoscopic view of the molecular structure, which indicates the atomic numbering scheme adopted and the thermal ellipsoids of the atoms, is given in Fig. 1. Bond distances and angles with their estimated deviations are given in Tables 5 and 6. The basic molecular structure is that of a binuclear complex of cobalt atoms coordinated by two η⁵-cyclopentadienyl ligands and a μ-bonded five-carbon atom ligand derived from each two molecules of diphenylacetylene and one of ethoxycarbonylcarbene.

The μ-bonded ligand is composed of C(11) and two olefinic functions derived from C(12) and C(13) and from C(14) and C(15). In the μ-bonded ligand, C(11) is bonded to a CO₂C₂H₅ group, C(15) is bonded to a phenyl and a CH₂CO₂C₂H₅

TABLE 4
IR AND NMR SPECTRA OF V AND VI

Compound	IR	NMR: δ ^b (multiplicity ^c , relative intensity, assignment) (ppm)			
	$\nu(\text{CO})$ (cm^{-1}) ^a	C_5H_5	R	Others	
Va	1716, 1705	4.59(s, 5)	3.39(s, 3, CH ₃)	2.95(d, <i>J</i> 18 Hz, 1, H—C—H), 3.56 (d, <i>J</i> 18 Hz, 1, H—C—H), 6.7—7.8(m, 20, Ph)	
		5.14(s, 5)	3.84(s, 3, CH ₃)		
Vb	1715, 1689	4.59(s, 5)	0.86(t ^d , 3, CH ₃)	2.93(d, <i>J</i> 18 Hz, 1, H—C—H), 3.56 (d, <i>J</i> 18 Hz, H—C—H, 1), 6.6—7.7(m, 20, Ph)	
		5.16(s, 5)	1.33(t ^d , 3, CH ₃)		
Vc	1702, 1668	4.58(s, 5)	3.85(dq ^e , 2, CH ₂)	2.85(d, <i>J</i> 18 Hz, H—C—H, 1), 3.52(d, <i>J</i> 18 Hz, 1, H—C—H), 6.6—7.8(m, 20, Ph)	
			4.30(q ^d , 2, CH ₂)		1.15(s, 9, (CH ₃) ₃ C)
			5.11(s, 5)		1.48(s, 9, (CH ₃) ₃ C)
Via	1712	5.23(s, 10)	3.61(s, 6, CH ₃)	2.72(s, 2, CH), 6.9—7.6(m, 20, Ph)	
Vib	1710, 1680	5.24(s, 10)	1.26(t ^d , 6, CH ₃)	2.82(s, 2, CH)	
			4.06(m ^e , 4, CH ₂)	6.9—7.5(m, 20, Ph)	
Vic	1705	5.25(s, 10)	1.42(s, 18, (CH ₃) ₃ C)	3.13(s, 2, CH), 6.9—7.5(m, 20, Ph)	

^a KBr pellet. ^b In CDCl₃. ^c s, singlet; d, doublet; t, triplet; q, quartet; dq, double quartet; m, multiplet. ^d *J* = 7 Hz. ^e Both the signals showed ABX₃ patterns (*J*_{AB} = 11 Hz, *J*_{AX} = *J*_{BX} = 7 Hz).

group, while C(12), C(13), and C(14) each are bonded to a phenyl group, respectively. The metal-to-ligand bonding can be described in terms of both σ -bonds (bridging) of C(11) to Co(1) and Co(2), and π -bonds between one olefinic function (C(12), C(13)) and Co(2) and between the other olefinic function (C(14), C(15)) and Co(1).

The bond distance (1.89(1) Å) between C(11) and Co(1) is somewhat shorter than that (1.95(1) Å) between C(11) and Co(2), and the angle Co(1)—C(11)—Co(2) is 82.8(4)°. The mode of bonding between Co(2) and the three carbon atoms

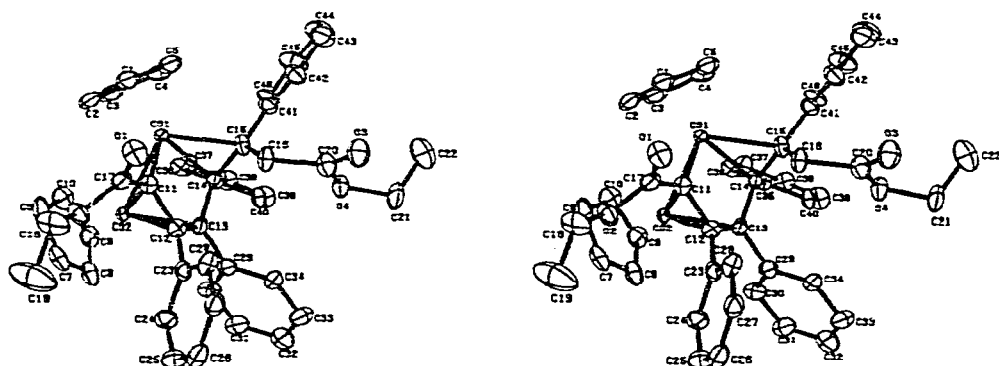


Fig. 1. A stereoscopic view of the molecular structure of Vb.

TABLE 5

SELECTED BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATION

Bond	Length	Bond	Length
Co(1)—Co(2)	2.532(2)	C(13)—C(29) [Ph]	1.51(2)
Co(1)—C(11)	1.89(1)	C(14)—C(35) [Ph]	1.52(2)
Co(1)—C(14)	2.08(1)	C(15)—C(41) [Ph]	1.49(2)
Co(1)—C(15)	2.13(1)	Co(1)—C(1)	2.10(1)
Co(2)—C(11)	1.95(1)	Co(1)—C(2)	2.11(1)
Co(2)—C(12)	1.99(1)	Co(1)—C(3)	2.14(1)
Co(2)—C(13)	2.05(1)	Co(1)—C(4)	2.14(1)
C(11)—C(12)	1.44(1)	Co(1)—C(5)	2.08(1)
C(12)—C(13)	1.47(2)	Co(2)—C(6)	2.11(1)
C(13)—C(14)	1.49(2)	Co(2)—C(7)	2.09(1)
C(14)—C(15)	1.46(2)	Co(2)—C(8)	2.08(1)
C(15)—C(16)	1.54(2)	Co(2)—C(9)	2.12(1)
C(11)—C(17)	1.49(2)	Co(2)—C(10)	2.12(1)
C(17)—O(1)	1.21(1)	C(1)—C(2)	1.39(2)
C(17)—O(2)	1.36(1)	C(2)—C(3)	1.43(2)
O(2)—C(18)	1.49(2)	C(3)—C(4)	1.42(2)
C(18)—C(19)	1.38(2)	C(4)—C(5)	1.45(2)
C(16)—C(20)	1.54(1)	C(5)—C(1)	1.36(2)
C(20)—O(3)	1.22(1)	C(6)—C(7)	1.46(2)
C(20)—O(4)	1.32(2)	C(7)—C(8)	1.42(2)
O(4)—C(21)	1.46(1)	C(8)—C(9)	1.41(2)
C(21)—C(22)	1.49(2)	C(9)—C(10)	1.46(2)
C(12)—C(23) [Ph]	1.48(2)	C(10)—C(6)	1.50(2)

TABLE 6

SELECTED BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATION

Bond	Angle	Bond	Angle
Co(2)—Co(1)—C(11)	49.7(3)	C(15)—C(14)—Co(1)	71.7(6)
Co(2)—Co(1)—C(14)	69.1(3)	C(15)—C(14)—C(13)	121.7(9)
Co(2)—Co(1)—C(15)	105.2(3)	Co(1)—C(14)—C(13)	102.9(7)
C(11)—Co(1)—C(14)	86.6(4)	C(15)—C(14)—C(25)	120.9(9)
C(11)—Co(1)—C(15)	96.4(5)	Co(1)—C(14)—C(35)	121.5(7)
C(14)—Co(1)—C(15)	40.4(4)	C(13)—C(14)—C(35)	111.1(8)
Co(1)—Co(2)—C(11)	47.6(3)	C(16)—C(15)—Co(1)	108.4(7)
Co(1)—Co(2)—C(12)	76.9(3)	C(16)—C(15)—C(14)	118.0(9)
Co(1)—Co(2)—C(13)	75.2(3)	C(16)—C(15)—C(41)	112.8(9)
C(11)—Co(2)—C(12)	43.0(4)	Co(1)—C(15)—C(14)	67.9(6)
C(11)—Co(2)—C(13)	73.3(4)	C(14)—C(15)—C(41)	125.2(9)
C(12)—Co(2)—C(13)	42.9(4)	C(20)—C(16)—C(15)	113.1(9)
C(12)—C(11)—Co(1)	116.5(7)	C(11)—C(17)—O(1)	127(1)
C(12)—C(11)—Co(2)	69.7(6)	C(11)—C(17)—O(2)	111(1)
C(12)—C(11)—C(17)	115.1(9)	O(1)—C(17)—O(2)	122(1)
Co(1)—C(11)—Co(2)	82.8(4)	C(19)—C(18)—O(2)	110(1)
Co(1)—C(11)—C(17)	126.7(8)	C(16)—C(20)—O(3)	123(1)
Co(2)—C(11)—C(17)	128.0(8)	C(16)—C(20)—O(4)	113(1)
C(13)—C(12)—Co(2)	71.1(6)	O(3)—C(20)—O(4)	124(1)
C(13)—C(12)—C(11)	110.1(9)	C(22)—C(21)—O(4)	110(1)
C(13)—C(12)—C(23)	125.0(9)	C(2)—C(1)—C(5)	111(1)
Co(2)—C(12)—C(11)	67.3(6)	C(3)—C(2)—C(1)	107(1)
Co(2)—C(12)—C(23)	130.9(8)	C(4)—C(3)—C(2)	108(1)
C(11)—C(12)—C(23)	124.9(9)	C(5)—C(4)—C(3)	106(1)
C(14)—C(13)—Co(2)	95.3(6)	C(1)—C(5)—C(4)	108(1)
C(14)—C(13)—C(12)	117.3(9)	C(7)—C(6)—C(10)	106(1)
C(14)—C(13)—C(29)	119.7(9)	C(8)—C(7)—C(6)	110(1)
Co(2)—C(13)—C(12)	66.1(6)	C(9)—C(8)—C(7)	108(1)
Co(2)—C(13)—C(29)	125.9(7)	C(10)—C(9)—C(8)	110(1)
C(12)—C(13)—C(29)	119.1(9)	C(6)—C(10)—C(9)	105(1)

C(11), C(12), and C(13) can be regarded as that of a π -allyl structure, and the fragment containing Co(1) is similar to those in "flyover" type complexes, such as, $\text{Co}_2(\text{CO})_4(\text{CF}_3\text{C}_2\text{H})_3$ (VIII) [6] and $\text{Co}_2(\text{CO})_4(t\text{-BuC}_2\text{H})_2(\text{HC}_2\text{H})$ (IX) [7], and $\text{Fe}_2(\text{CO})_6[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{C}(\text{OCH}_3)\text{CH}=\text{CHC}(\text{OCH}_3)]$ [8]. The Co(2)—C(11) (1.95(1) Å), Co(2)—C(12) (1.99(1) Å), and Co(2)—C(13) (2.05(1) Å) distances are comparable with the corresponding Co—C distances (1.95(3), 2.05(3), and 2.11(3); 1.95(3), 2.06(3), and 2.02(3) Å) observed for VIII and the Co(1)—C(11) distance is shorter than those (1.96(3) and 1.98(3) Å) observed for VIII. Within the allylic group (C(11), C(12), and C(13)) the mean distance (1.46 Å) is slightly longer than those (1.39 and 1.44 Å) for VIII and the C(11)—C(12)—C(13) angle ($110.4(9)^\circ$) is in good agreement with the corresponding angles ($108.7(2.5)$ and $114.5(2.0)^\circ$) observed for VIII.

The bonding of the olefinic function (C(14), C(15)) to C(1) is supported by the long C(14)—C(15) distance (1.46(2) Å) and the Co(1)—C(14) (2.08(1) Å) and the Co(1)—C(15) (2.13(1) Å) distances.

The methylenic carbon C(16) which is bonded to C(15) is bonded also to an ethoxycarbonyl group and two hydrogen atoms. One of these hydrogen atoms may have been bonded originally to C(11) in an intermediate on the way to formation of V. The bond distances and bond angles about C(16) are consistent with a normal sp^3 hybridized carbon atom.

The two cobalt atoms are separated by 2.532(2) Å. This distance is similar to that observed for $\text{Co}_2(\text{CO})_8$ (2.524 Å) [9] and $\text{Co}_2(\text{CO})_6(\pi\text{-norbornadiene})$ (2.531 Å) [10], and is slightly longer than that distance in $\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})$ (2.47 Å) [11], VIII (2.459 Å), and IX (2.45 Å).

Both cyclopentadienyl rings are planar and the average values of the C—C bond distances within each ring are 1.41 and 1.45 Å. The average value of the Co—C distances for both rings are 2.11 Å. The dihedral angle between the two rings is 87.1° , which is in good agreement with that (87.7°) for $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$ [12].

As mentioned above, the ^1H NMR spectra of V indicate the presence of two kinds of the alkoxycarbonyl groups, having widely separated resonances. The signals which appear at lower field (Va, δ 3.84; Vb*, 4.30 (q, CH_2) and 1.33 (t, CH_3); Vc, 1.48 ppm) are assigned to the $\text{CH}_2\text{CO}_2\text{R}$ groups because the chemical shifts are fairly consistent with those of alkyl acetates ($\text{CH}_3\text{CO}_2\text{R}$, δ 3.67 (R = CH_3); 4.05 and 1.21 (R = C_2H_5); 1.45 ppm (R = $\text{C}(\text{CH}_3)_3$) [13]. Therefore, those resonances which appear at higher field (Va, δ 3.39; Vb*, 3.85 (dq**, CH_2) and 1.33 (t, CH_3); Vc, 1.15 ppm) should be assigned to the alkoxycarbonyl groups on carbon C(11) which bridges the two cobalt atoms. It would seem that these upfield shifts are mainly due to the anisotropic effect of the benzene ring on the carbon C(12), which is *cis* to the alkoxycarbonyl groups as shown by the molecular structure determination of V_U (Fig. 1).

In connection with the structure of V, the complex VI may be regarded as a bis(π -allylic) complex in which two sets of three carbon atoms in the hexatrienic

* The correspondence of these signals in the ethyl groups was proved by a double resonance technique.

** Appearance of the methylene protons as a double quartet is due to the presence of a chiral center at C(11).

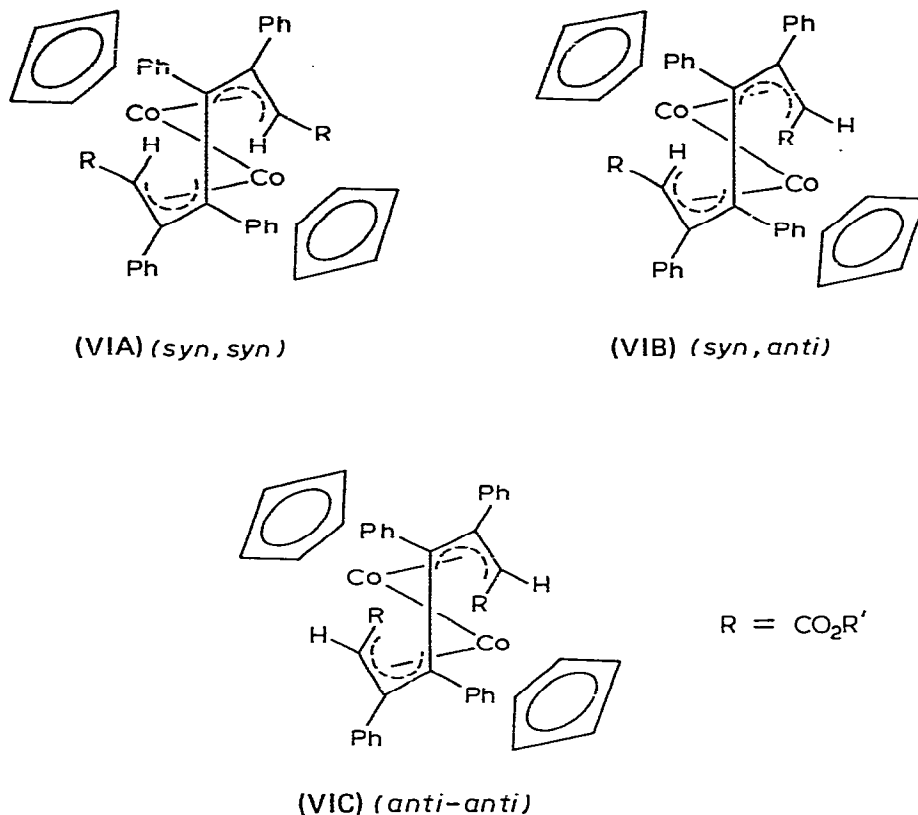
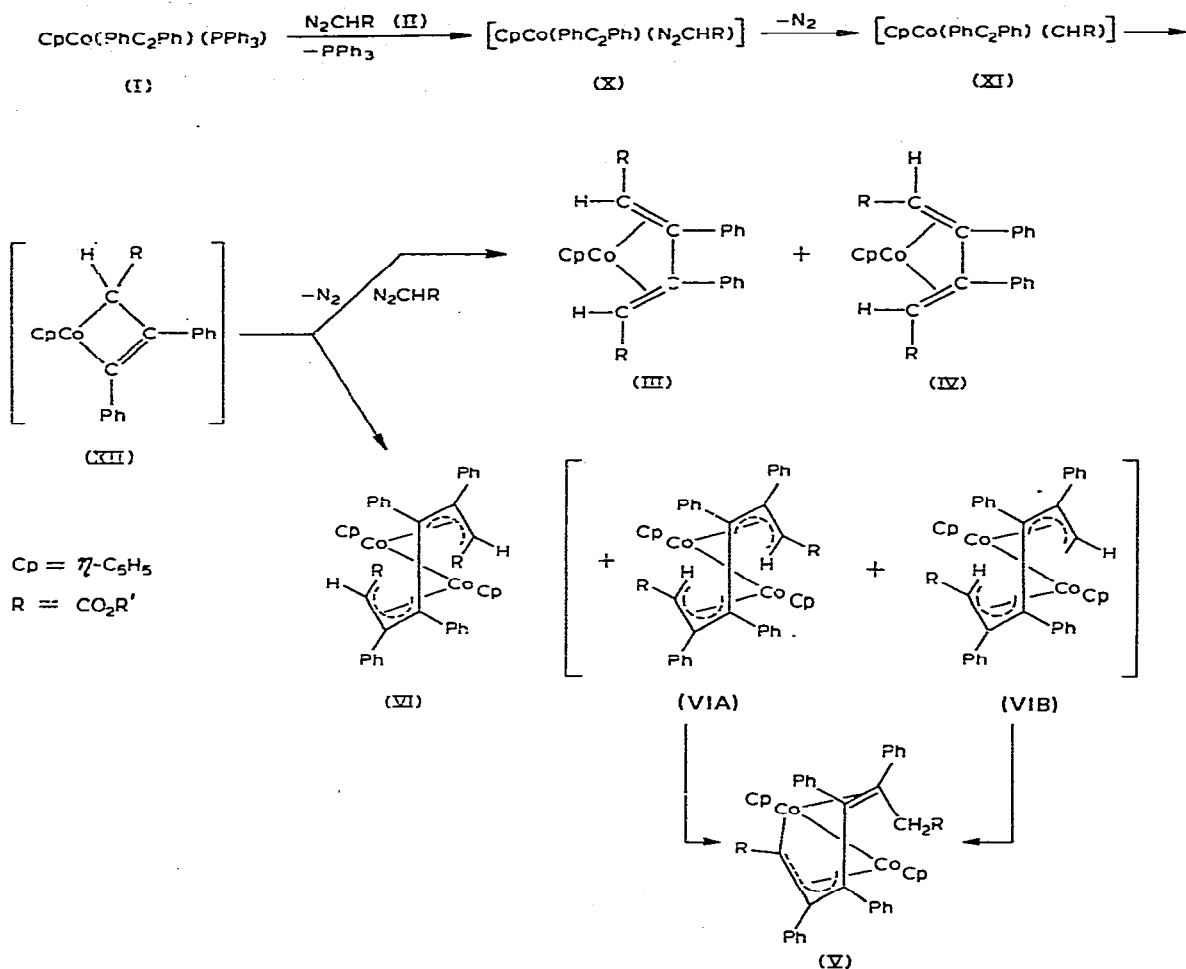


Fig. 2. Possible structures for VI.

skeleton coordinate to each cobalt atom. There are three possible forms of the bis(π -allylic) structure as shown in Fig. 2; *syn, syn* (VIA) *syn, anti* (VIB), and *anti, anti* (VIC) forms. Among these forms the *syn, anti*-structure (VIB) was ruled out, because it could not account for the equivalency of the cyclopentadienyl and alkoxy carbonylmethylene groups. The chemical shifts of the alkoxy carbonyl groups are similar to those for the groups which are *trans* to neighboring phenyl substituents in IV rather than those which are *cis*, as in III, IV, and V. For example, the chemical shift (δ 1.42 ppm) of the *t*-butyl group in VIC is similar to that (δ 1.47 ppm) of the *anti* $\text{CO}_2\text{C}(\text{CH}_3)_3$ group in IVc rather than those (δ 1.15, 1.25, and 1.24 ppm) for the *syn*- $\text{CO}_2\text{C}(\text{CH}_3)_3$ group in IIIc, IVc, and Vc. Therefore, we finally propose the structure of VI to the *anti, anti* structure (VIC).

The formation of all of the products obtained from the reaction of I with II can be reasonably explained by the assumption of the intermediate formation of the cobaltacyclobut-2-ene complexes XII, which is similar to the formation of the 3-iminocobaltacyclobut-2-ene complexes in reactions of I with isocyanides [2]. As shown in the Scheme 1 alkyl diazoacetates displace the triphenylphosphine of I in the first step, followed by the elimination of dinitrogen from the coordinated alkyl diazoacetates to give carbene complexes XI, which convert

SCHEME 1



to the cobaltacyclobut-2-enes XII. The dimerization of XII might give three possible isomers of bis(π -allyl) complexes VIA–VIC. Among these isomers, the *syn,syn* and *syn,anti* isomers (VIA and VIB) were not obtained. This result suggests that VIA and VIB isomerize readily to the product V by the migration of a hydrogen atom on a terminal carbon atom in the hexatriene skeleton to the other terminal carbon atom. The ready migration of the hydrogen atom is probably due to the atom being directed at the cobalt atom which binds with the other π -allylic function. On the other hand, the *anti,anti* isomer (VIC) does not isomerize to V because both the hydrogen atoms at the terminal carbon atoms are not directed at the cobalt atoms. The low yield of VI probably can be attributed to the steric interaction between the alkoxy carbonyl groups and the cobalt atoms.

To the coordinated unsaturated intermediate XII, further attack of II, followed by the elimination of dinitrogen, gives the diene complexes III and IV. In this reaction the *anti,anti* isomer was not detected, probably because of unfavourable steric interactions.

(Continued on p. 291)

TABLE 7

ATOMIC PARAMETERS WITH THEIR STANDARD DEVIATIONS

	x	y	z
Co(1)	0.0374(1)	0.0615(1)	0.1842(1)
Co(2)	0.1553(1)	0.0191(1)	0.2183(1)
C(1)	-0.0568(6)	0.0214(7)	0.2172(7)
C(2)	-0.0146(6)	-0.0271(6)	0.1897(7)
C(3)	-0.0017(7)	-0.0124(7)	0.1128(8)
C(4)	-0.0345(7)	0.0464(6)	0.0959(7)
C(5)	-0.0676(6)	0.0675(6)	0.1644(7)
C(6)	0.1495(9)	-0.0807(5)	0.2372(9)
C(7)	0.2092(7)	-0.0530(6)	0.2739(7)
C(8)	0.2521(7)	-0.0232(6)	0.2204(7)
C(9)	0.2237(7)	-0.0334(6)	0.1491(7)
C(10)	0.1579(7)	-0.0670(6)	0.1558(8)
C(11)	0.0820(5)	0.0570(5)	0.2775(6)
C(12)	0.1442(5)	0.3937(5)	0.2853(6)
C(13)	0.1675(5)	0.1165(4)	0.2117(6)
C(14)	0.1139(5)	0.1261(5)	0.1531(6)
C(15)	0.0512(6)	0.1621(5)	0.1680(6)
C(16)	0.0443(6)	0.1957(5)	0.2442(6)
C(17)	0.0521(6)	0.0329(5)	0.3488(7)
C(18)	0.0779(7)	-0.0278(8)	0.4598(7)
C(19)	0.1380(10)	-0.0427(13)	0.4964(10)
C(20)	0.0505(6)	0.2691(5)	0.2390(7)
C(21)	0.1122(8)	0.3566(6)	0.1862(8)
C(22)	0.0598(10)	0.3874(7)	0.1375(8)
C(23)	0.1777(6)	0.1095(5)	0.3574(6)
C(24)	0.2472(6)	0.0934(6)	0.3717(6)
C(25)	0.2767(6)	0.1094(6)	0.4398(7)
C(26)	0.2385(7)	0.1411(6)	0.4945(7)
C(27)	0.1699(7)	0.1567(5)	0.4813(6)
C(28)	0.1417(6)	0.1414(5)	0.4115(6)
C(29)	0.2353(5)	0.1517(5)	0.2059(6)
C(30)	0.2913(6)	0.1292(6)	0.1669(6)
C(31)	0.3508(6)	0.1671(6)	0.1599(7)
C(32)	0.3528(7)	0.2277(6)	0.1919(7)
C(33)	0.2955(6)	0.2504(6)	0.2311(8)
C(34)	0.2372(6)	0.2129(5)	0.2385(7)
C(35)	0.1453(5)	0.1248(5)	0.0755(6)
C(36)	0.1425(6)	0.0718(5)	0.0278(6)
C(37)	0.1644(7)	0.0754(6)	-0.0459(6)
C(38)	0.1967(7)	0.1312(6)	-0.0697(6)
C(39)	0.2032(7)	0.1844(6)	-0.0225(6)
C(40)	0.1796(6)	0.1806(5)	0.0491(6)
C(41)	0.0053(6)	0.1899(5)	0.1101(6)
C(42)	-0.0543(6)	0.2213(6)	0.1336(6)
C(43)	-0.1012(7)	0.2506(8)	0.0859(8)
C(44)	-0.0890(8)	0.2465(8)	0.0072(8)
C(45)	-0.0311(8)	0.2140(8)	-0.0179(8)
C(46)	0.0147(6)	0.1866(6)	0.0309(6)
O(1)	0.0003(4)	0.0516(4)	0.3785(4)
O(2)	0.0932(4)	-0.0121(4)	0.3802(4)
O(3)	0.0165(5)	0.3052(4)	0.2776(5)
O(4)	0.0986(4)	0.2879(3)	0.1915(5)

TABLE 8

ANISOTROPIC THERMAL PARAMETERS ($\times 10^{-4}$) WITH THEIR STANDARD DEVIATIONS^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	14(0)	11(0)	14(0)	-2(0)	-0(0)	0(0)
Co(2)	15(C)	9(0)	16(0)	1(0)	2(0)	-0(0)
C(1)	23(4)	30(4)	30(4)	-4(3)	3(4)	-1(4)
C(2)	31(4)	23(3)	41(5)	-10(3)	-6(4)	-0(4)
C(3)	27(4)	33(4)	47(6)	-6(4)	-3(4)	-10(4)
C(4)	36(5)	36(4)	35(5)	-9(4)	-23(4)	0(4)
C(5)	21(4)	31(4)	41(5)	-6(3)	-8(4)	-0(4)
C(5)	62(7)	13(3)	64(8)	9(4)	-7(6)	-1(4)
C(7)	41(5)	24(4)	35(5)	15(4)	4(4)	6(4)
C(8)	32(4)	20(3)	43(5)	5(3)	4(4)	0(4)
C(9)	36(5)	22(3)	40(5)	8(3)	3(4)	-7(4)
C(10)	36(5)	20(3)	58(5)	7(4)	10(5)	-14(4)
C(11)	25(3)	17(3)	20(3)	0(3)	2(3)	-3(3)
C(12)	19(3)	16(2)	25(4)	4(2)	3(3)	-4(3)
C(13)	22(3)	14(2)	25(4)	-1(2)	4(3)	2(3)
C(14)	21(3)	12(2)	23(4)	-0(2)	-0(3)	3(3)
C(15)	27(4)	13(3)	32(5)	6(3)	5(4)	-0(3)
C(16)	28(4)	16(3)	24(4)	3(3)	3(4)	-0(3)
C(17)	24(4)	17(3)	36(4)	-2(3)	4(3)	-0(3)
C(18)	25(5)	7(3)	23(4)	-13(5)	-5(4)	31(5)
C(19)	56(8)	142(15)	39(7)	8(9)	-2(5)	33(9)
C(20)	30(4)	20(3)	35(5)	0(3)	9(4)	5(3)
C(21)	53(6)	14(3)	56(7)	-3(3)	9(6)	4(4)
C(22)	35(9)	31(5)	46(7)	20(5)	15(7)	13(5)
C(23)	31(4)	13(3)	26(4)	0(3)	0(3)	4(3)
C(24)	26(4)	26(3)	23(4)	0(3)	-0(3)	1(3)
C(25)	30(4)	30(4)	34(5)	-0(3)	-3(4)	-5(4)
C(26)	40(5)	20(3)	30(5)	-10(3)	-1(4)	-3(3)
C(27)	39(5)	17(3)	26(4)	-2(3)	-9(4)	-2(3)
C(28)	31(4)	18(3)	31(5)	-3(3)	-1(4)	2(3)
C(29)	20(3)	22(3)	22(4)	-0(3)	-0(3)	2(3)
C(30)	22(4)	31(4)	22(4)	2(3)	2(3)	6(3)
C(31)	28(4)	30(4)	32(5)	-6(3)	2(4)	3(3)
C(32)	32(4)	36(4)	38(5)	-2(4)	6(4)	9(4)
C(33)	28(4)	24(3)	53(7)	-8(3)	-9(5)	-3(4)
C(34)	19(4)	21(3)	51(5)	-1(3)	-0(3)	-4(3)
C(35)	22(4)	13(2)	24(4)	-0(3)	2(3)	-0(3)
C(36)	28(4)	21(3)	21(4)	4(3)	3(3)	0(3)
C(37)	37(5)	24(3)	27(4)	-5(3)	11(4)	-2(3)
C(38)	38(5)	31(4)	21(4)	2(4)	7(4)	-0(3)
C(39)	45(5)	32(4)	22(5)	-2(4)	10(4)	9(4)
C(40)	38(5)	12(3)	26(4)	-0(3)	4(4)	8(3)
C(41)	21(4)	21(3)	25(4)	0(3)	-2(3)	8(3)
C(42)	28(4)	31(4)	28(4)	10(3)	3(4)	8(3)
C(43)	33(5)	41(5)	48(7)	7(4)	-2(5)	10(5)
C(44)	36(5)	54(5)	37(6)	4(5)	-8(5)	16(5)
C(45)	38(6)	55(6)	44(6)	9(5)	-10(5)	19(5)
C(46)	29(4)	30(4)	25(4)	13(3)	-3(4)	3(4)
C(1)	35(3)	30(3)	32(3)	4(2)	10(3)	4(2)
O(2)	33(3)	27(2)	31(3)	6(2)	-0(2)	10(2)
O(3)	45(4)	23(2)	44(4)	3(2)	11(3)	-5(3)
O(4)	37(3)	14(2)	46(4)	2(2)	9(3)	0(2)

^a β_{ij} is defined by: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{13} + 2kl\beta_{43})]$.

Experimental

All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Mitamura capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer. ^1H NMR spectra were obtained on Varian HA-100B spectrometer using tetramethylsilane as an internal reference. Mass spectra were measured on a Nippondenshi JPS-IS mass spectrometer with direct inlet system at 75 eV electron energies. The acetylene complex, $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})$ (I) [14], and ethyl [15] and *t*-butyl diazoacetate [16] were prepared according to published methods. Methyl diazoacetate was prepared from methyl α -diazoacetoacetate in a similar manner for synthesis of *t*-butyl analog.

Reaction of $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})$ (I) with ethyl diazoacetate

To a solution of I (570 mg, 1 mmol) in benzene (20 ml) was added ethyl diazoacetate (250 mg, 2.2 mmol), and the mixture was stirred at room temperature. Nitrogen gas was slowly evolved, and the solution gradually changed from green to brownish-red. After it has stood overnight, the brownish-red solution was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica (Wakogel C-200, ϕ 2.5 cm \times 20 cm). Two brown zones and two red zones were observed. From the first brown fraction which was eluted with benzene/ethyl acetate (100/1), a very small amount (<1 mg) of dark brown crystals, VIb, was obtained. The second brown fraction was eluted with benzene/ethyl acetate (100/2) and the solvent was removed under reduced pressure. After the addition of ethanol (2 ml), the solution was kept at room temperature to give dark brown crystals of Vb (177 mg, 46%).

The third and fourth red zones were eluted with 100/3 and 100/5 mixtures of benzene and ethyl acetate, respectively. By similar procedures to that above, red crystals of IIIb (80 mg, 17%) from the third zone and red crystals of IVb (45 mg, 10%) from the fourth zone were obtained.

Similarly, the reactions of I with methyl and *t*-butyl diazoacetates were made and all the products could be isolated.

The decomposition of IVa with ceric ammonium nitrate

To a stirred solution of IVa (223 mg, 0.5 mmol) in benzene (10 ml) and ethanol (5 ml) was added ceric ammonium nitrate (1 g) at room temperature, and the mixture was stirred for 15 min. After removal of the solvent under reduced pressure, the residue was extracted with benzene (20 ml). The extract was chromatographed on silica. The fraction eluted with benzene/dichloromethane (3/1) was collected. After removal of the solvent, the residue was recrystallized from benzene/hexane to give colorless crystals of dimethyl *trans,cis*-2,3-diphenylmuconate (VII) (120 mg, 75%), m.p. 90–91°C. Found: C, 74.48; H, 5.61, $\text{C}_{20}\text{H}_{18}\text{O}_4$ calcd.: C, 74.52; H, 5.64%. M^+ m/e 322 (calcd. 322). ^1H NMR spectrum (CDCl_3): δ 3.61 (s, 3H, O—CH₃), 3.67 (s, 3H, O—CH₃), 6.02 (s, 1H, =CH), 6.17 (s, 1H, =CH) and 7.1–7.6 ppm (m, 10H, C₆H₅).

X-ray structure determination

Recrystallization of compound Vb from benzene/ethanol gave well-formed

crystals suitable for X-ray studies. Precession and Weissenberg photography established that the crystals were orthorhombic with the systematic absences of $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, consistent with space group $Pbca$. Cell constants of a 19.466(7), b 20.843(7), and c 17.921(6) Å at 20°C were determined from high-order reflections on a Phillips PW1100 four-circles automated diffractometer.

The crystal with six faces of the forms $\{100\}$, $\{010\}$, and $\{001\}$ was mounted such that the a axis was nearly parallel to the ϕ axis of a diffractometer. The perpendicular distances to each of these faces were 0.0665, 0.0163, and 0.0128 cm, respectively.

Intensities were measured by the $2\theta - \omega$ scan method using $\text{Mo-K}\alpha$ radiation monochromated by a graphite crystal. A scan rate of 4° min^{-1} was used. Ten second stationary background counts were taken at the lower and upper limits of each scan. Three standard reflections were monitored before every 180 measurements. A total of 2666 independent intensities for which $F_o \geq 3\sigma(F_o)$ were obtained in the range $2\theta < 50^\circ$, and used in the solution and refinement of the structure.

The intensities were corrected for Lorentz, polarization, and absorption effects (the linear absorption coefficients of this compound for $\text{Mo-K}\alpha$ radiation is 9.84 cm^{-1} and the calculated transmission factors varied from 0.801 and 0.844).

Solution and refinement of structure

Two cobalt atoms were located from a three-dimensional Patterson map. A subsequent Fourier map phased by two cobalt atoms gave the positions of the remaining non-hydrogen atoms.

Five cycles of block-diagonal least-squares refinement of all the positional and isotropic thermal parameters resulted in the residual factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ of 11.1 and 12.9%, respectively. Five further cycles of refinement with anisotropic thermal parameters converged to $R_1 = 7.4\%$ and $R_2 = 8.3\%$. A difference Fourier synthesis revealed 40 of the 42 hydrogen atoms. Four more cycles of block-diagonal least-squares calculations completed the refinement, in which the 40 hydrogen atoms were included. The hydrogen atoms were given isotropic thermal parameters. This refinement converged to the lower residual factors $R_1 = 6.50\%$ and $R_2 = 7.21\%$. In these refinements, the $\Sigma w(|F_o| - |F_c|)^2$ function was minimized, where the weight, w , was $1/\sigma(F_o)$. No unusual trends were observed in an analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of either $\sin \theta/\lambda$ or $|F_o|$. Anomalous dispersion effects were included in the calculation of F_c using f' and f'' calculated by Cromer [17]. The atomic scattering factors for Co, C, O and H were from the usual tabulation [18].

The final atomic coordination and thermal parameters are listed in Table 7 and 8. The table of structure factors has been deposited*.

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