Cobalt Metallocycles. 6.[1] Preparation and Structure of Cobaltacyclopentene Complexes and Their Reactions with Olefins and Acetylenes

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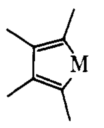
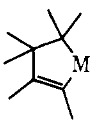
Abstract: (η^2-Acetylene)(η^5-cyclopentadienyl)(triphenylphosphine)cobalt, $Co(C_5H_5)(R^1C{\equiv}CR^2)(PPh_3)$ (**1**), where R^1 = Ph or CO_2Me, R^2 = CO_2Me, reacts with 1,2-disubstituted olefins (dimethyl maleate, dimethyl fumarate, fumaronitrile, crotononitrile) to form novel metallocyclopentene complexes, $(\eta^5\text{-}C_5H_5)(PPh_3)(\overline{CoCR^1{=}CR^2CHR^3CHR^4})$ (**2**). A kinetic study indicates an intermediate in which acetylene and olefin are simultaneously coordinated to cobalt. One of the cobaltacyclopentene complexes, **2a** (R^1 = Ph; $R^2 = R^3 = R^4 = CO_2Me$), has been characterized by an X-ray crystal-structure analysis. In contrast, monosubstituted olefins (acrylonitrile, methyl acrylate) react with **1** to give cobalt-diene complexes of the composition $Co(C_5H_5)[(acetylene)(olefin)_2]$ (**4**). That these compounds (**4**) are presumably formed via cobaltacyclopentene intermediates is evidenced by the fact that a similar diene complex is formed when **2a** is reacted with acrylonitrile Diphenylacetylene and acrylonitrile cotrimerize in the presence of a catalytic amount of $Co(C_5H_5)(PhC_2Ph)(PPh_3)$ (**1c**) to give a linear diene of the composition $(PhC_2Ph)(CH_2CHCN)_2$. The reaction of **2a** with acetylenes yields cobalt–cyclohexadiene complexes.

Transition metal catalyzed cyclic or linear 2:1 cooligomerization of acetylene with olefin has been documented by several workers. Chalk has examined $Ni(CO)_2(PPh_3)_2$ catalyst for 2:1 cyclotrimerization of substituted acetylenes with maleimide and obtained cyclohexadiene derivatives.[2] Similar reactions have been reported to occur in the presence of $Fe(C_8H_8)_2$,[3] $[(C_2H_4)_2RhCl]_2$,[4] and $\{Pd[C_4(CO_2Me)_4]\}_m$.[5] Cairns et al. have shown that $Ni(CO)_4/PPh_3$ is an effective catalyst for the 2:1 linear cotrimerization of acetylene with acrylic compounds.[6] Among many mechanisms imaginable for these reactions, at least for the cyclotrimerization, the one with metallocyclopentadiene intermediacy (I) appears most likely because a number of metallocyclopentadiene complexes have been isolated by the reaction of two acetylene molecules with low-valent transition metal complexes.[7] Furthermore, cobaltacyclopentadiene complexes thus obtained have been demonstrated to react with olefins to give cyclohexadiene and/or cyclohexadiene complexes.[8] The isolation of a palladiacyclopentadiene complex coordinated with diolefin, which may be regarded as an intermediate in this type of cooligomerization, has also been reported.[5]



I

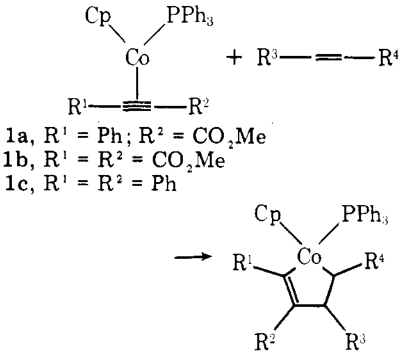


II

In a previous communication we reported hitherto unknown linear 1:2 cooligomerization of diphenylacetylene with acrylonitrile catalyzed by a cobalt complex and presented a reaction path involving a cobaltacyclopentene intermediate (II) which corresponded to I in 2:1 cooligomerization reactions mentioned above.[9] In this paper, we wish to describe in more detail the formation of this novel metallocycle from acetylene and olefin together with its characteristic reactions which are relevant to the mechanism for alkyne–alkene cooligomerization.

Results and Discussion

Formation of Cobaltacyclopentene Complexes. (η^2-Methyl phenylpropiolate)(η^5-cyclopentadienyl)(triphenylphosphine)cobalt (**1a**) and its dimethyl acetylenedicarboxylate analogue (**1b**) reacted at ambient temperature with disubstituted olefins such as dimethyl maleate, dimethyl fumarate, fumaronitrile, and crotononitrile to form the cobaltacyclopentene complexes (**2a–e**). Trans-disubstituted olefins (dimethyl fumarate, fumaronitrile, crotononitrile) led to a mixture of two isomeric cobaltacyclopentenes (the cases of **2b, 2d,** and **2e**) whereas the cis olefin (dimethyl maleate) yielded only one isomer (**2a** and **2c**). The physical and spectral data of thus obtained cobaltacyclopentenes are given in Table I.



1a, R^1 = Ph; R^2 = CO_2Me
1b, $R^1 = R^2 = CO_2Me$
1c, $R^1 = R^2$ = Ph

(1a)

2a, R^1 = Ph; $R^2 = R^3 = R^4 = CO_2Me$ (R^3, R^4 cis)
2b, R^1 = Ph; $R^2 = CO_2Me$; R^3 = Me; R^4 = CN (R^3, R^4 trans)
2c, $R^1 = R^2 = R^3 = R^4 = CO_2Me$ (R^3, R^4 cis)
2d, $R^1 = R^2 = R^3 = R^4 = CO_2Me$ (R^3, R^4 trans)
2e, $R^1 = R^2 = CO_2Me$; $R^3 = R^4$ = CN (R^3, R^4 trans)

The structure of **2a** was determined by a single-crystal X-ray analysis as shown in Figure 1. The two methoxycarbonyl groups, originating from dimethyl maleate, are located in the direction of the Cp ring (Figure 2 (C)). Complex **2c** must have an identical configuration. The two isomers present in **2d** and **2e** were thus assigned the general structure illustrated in Figure 2, (T-1) and (T-2). Although the NMR resonances attributable to the cobaltacyclopentene ring protons in **2a** were partially hidden by the CO_2Me absorptions, a careful examination of the spectrum revealed the presence of two double doublets centered at δ 3.42 (J_{HH} = 8, $J_{PH} \sim 14$ Hz) and 3.64 (J_{HH} = 8, J_{PH} = 2 Hz). The peak with $J_{PH} \sim 14$ Hz was attributed to the proton of shorter P-H distance, i.e., H^1, and the other to H^2 in configuration (C). In the spectrum of **2c,** the J_{PH^1} value of 14 Hz, as well as J_{PH^2} of 2 Hz, were unambiguously determined. The isomers in **2d** could be separated by column chromatography. One of them showed two double doublets at δ 2.74 (J_{HH} = 11, J_{PH} = 13 Hz) and 4.35 (J_{HH} = 11, J_{PH} = 4 Hz). Since the value of J_{PH^1} is essentially equal to those of **2a** and **2c** these were assigned to isomer **2dT-1.** The other isomer, **2dT-2,** showed an expected value of $J_{H^1H^2}$ (11 Hz), while its J_{PH^1} was only 2 Hz. A strong dependence of J_{PH^1} value on the direction of H at the α carbon has also been noticed in a related cobalt–fumaronitrile complex.[10] Although the isomers in **2e**

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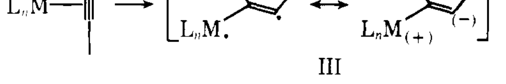
Table I. Physical Properties and Analytical Data of Cobaltacyclopentene Complexes (**2**), $(\eta^5\text{-}C_5H_5)(PPh_3)(\overline{CoCR^1{=}CR^2CHR^3}CHR^4)$

compd	yield, %	melt with dec, °C	anal. (calcd), %	NMR in CDCl$_3$, δ ppm[a] C_5H_5	CO_2Me	ring proton	
2a	30	177–178	C, 68.32 (67.83)	4.70	3.79	3.64 (d, d, J_{HH} = 8 Hz J_{PH} = 2 Hz)	
			H, 5.51 (5.25)		3.55	3.42 (d, d, J_{PH} = 14 Hz)	
					3.29		
2b[b]	7	162–164	C, 73.76 (73.61)[c]	4.70	3.32	2.9–3.1 (m)	1.42 (Me, d, J = 7 Hz)
			H, 5.61 (5.56)	4.64	3.30	1.2–1.3 (m)	0.95 (Me, d, J = 7 Hz)
			N, 1.85 (2.15)				
2c	64	178–179	C, 63.23 (62.51)	4.89	3.71	3.39 (d, d, J_{HH} = 8 Hz J_{PH} = 2 Hz)	
			H, 5.19 (5.10)		3.67	2.83 (d, d, J_{PH} = 14 Hz)	
					3.56		
					3.04		
2dT-1	29	213–214	C, 62.34 (62.51)	4.82	3.71	4.35 (d, d, J_{HH} - 11 Hz J_{PH} = 4 Hz)	
			H, 5.10 (5.10)		3.58	2.74 (d, d, J_{PH} = 13 Hz)	
					3.40		
					3.02		
2dT-2	11	oil	*d*	4.92	3.55	3.4–3.6 (?)[e]	
					3.53	2.64 (d, d, J_{HH} = 11 Hz J_{PH} = 2 Hz)	
					3.49		
					3.46		
2e[f]	18	177–183	C, 66.11 (65.35)	T-1 4.96	3.69	4.36 (d, d, J_{HH} = 11 Hz J_{PH} = 4.5 Hz)	
			H, 4.86 (4.65)		3.13	2.08 (d, d, J_{PH} = 13 Hz)	
			N, 4.34 (4.62)	T-2 5.01	3.62	3.98 (d, d, J_{HH} = 11 Hz J_{PH} = 3 Hz)	
					3.38	1.53 (d, d, J_{PH} = 2 Hz)	

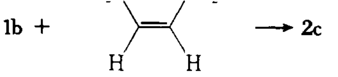
[a] Phenyl absorptions are omitted. [b] A 4:1 mixture of T-1 and T-2 isomers. [c] Solvated with $\frac{1}{2}C_6H_6$. [d] Analysis was not made. [e] Masked by CO_2Me peaks. [f] A 2:3 mixture of T-1 and T-2 isomers.

could not be separated, the NMR spectrum of their mixture was in full agreement with the above interpretations (see Table I). For **2b**, which was prepared by the reaction of **1a** with crotononitrile, eight isomers (four regio- with two stereoisomers) are possible, but actually only two isomers resulted from the reaction. These were tentatively assumed to have a common regiostructure indicated in eq 1a with two stereoisomers, T-1 and T-2.

For the formation of cobaltacyclopentene complex, two alternative reaction paths may be considered. The first of these involves an intermediate in which the phosphine is lost and acetylene and olefin are simultaneously coordinated to cobalt. The second one includes η^1-acetylene intermediate (III) without the loss of ligands.[11] In order to distinguish these, reaction 1b was followed by NMR with and without the addition

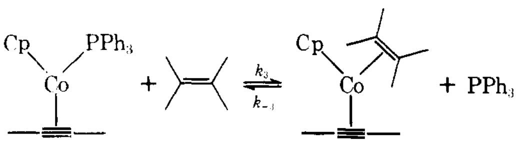


III



(1b)

of PPh$_3$. The reaction rate observed was consistent with the mechanism outlined in eq 2–4, i.e., the first reaction path mentioned above.



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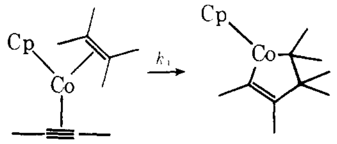
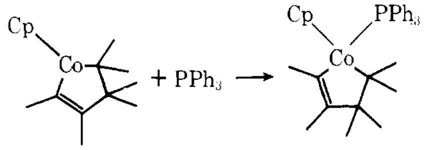


(3)



(4)

The observed reaction rate fitted the expression

$$\frac{(\mathrm{d}z)}{\mathrm{d}t} = \frac{\mathrm{d}(\mathbf{2c})}{\mathrm{d}t} = \frac{k_3k_4(a-z)(b-z)}{k_{-3}(c)+k_4}$$

$$\text{or } \frac{1}{(b-a)}\ln\frac{(a)(b-z)}{(b)(a-z)} = \frac{k_3k_4}{k_{-3}(c)+k_4}t \quad (5)$$

where (a), (b), and (c) are the initial concentrations of acetylene complex (**1b**), the olefin, and triphenylphosphine, respectively. Figure 3 shows the fit to eq 5 which gives the following values.

$$k_3 = 1.4 \times 10^{-2}\ \mathrm{M\ s^{-1}},\ k_{-3}/k_4 = 0.5 \times 10^5\ \mathrm{M^{-1}}$$

The mechanism indicated by eq 2–4 is essentially similar to the scheme suggested previously for the formation of cobaltacyclopentadienes from acetylene complex and acetylenes.[7]

The cobaltacyclopentene complex was not formed by another route, i.e., the reaction of olefin complex with acetylene. Thus (η^5-cyclopentadienyl)(η^2-dimethyl maleate)(triphenylphosphine)cobalt was treated with methyl phenylpropiolate or dimethyl acetylenedicarboxylate at room temperature, but only the olefin complex was recovered, suggesting that the

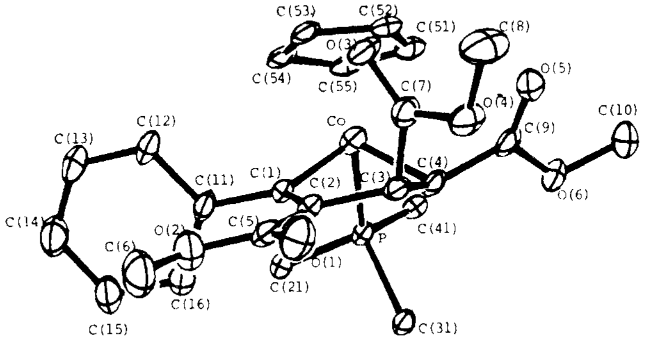
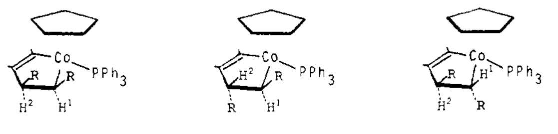


Figure 1. Molecular geometry of **2a**. The three phenyl rings of the phosphine have been omitted with only the first atoms C(21), C(31), and C(41) being shown.



C T-1 T-2

Figure 2. Configuration of the cobaltacyclopentene complexes derived from cis- and trans-disubstituted olefins.

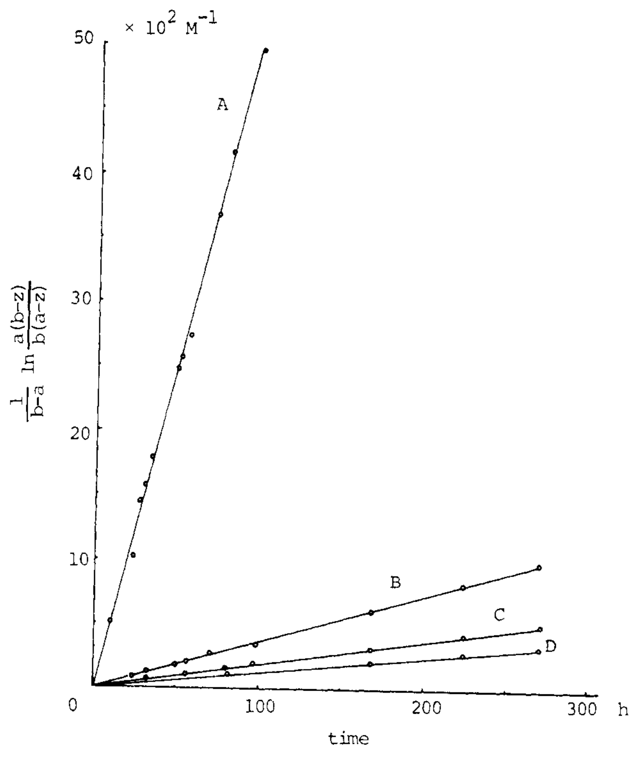
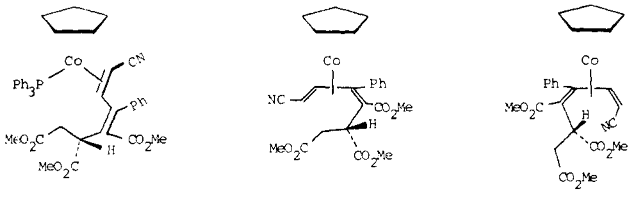
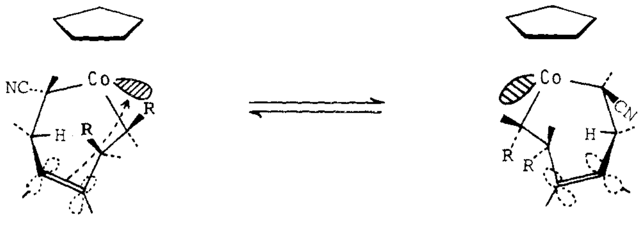


Figure 3. The effect of PPh_3 on the rate of cobaltacyclopentene formation from acetylene complex **1b**, 0.5×10^{-4} M, and dimethyl maleate, 5.0×10^{-4} M: (A) no PPh_3, (B) 0.25×10^{-4} M, (C) 0.5×10^{-4} M, (D) 0.75×10^{-4} M PPh_3.



3a 4a-1 4a-2

Figure 4. Cobalt-diene complexes formed by the reaction of **2a** with acrylonitrile.



9-1 9-2

Figure 5. Diastereoisomers of coordinatively unsaturated cobaltacycloheptene: R = CO_2Me.

displacement of the phosphine in the olefin complex by acetylene does not occur under these conditions.

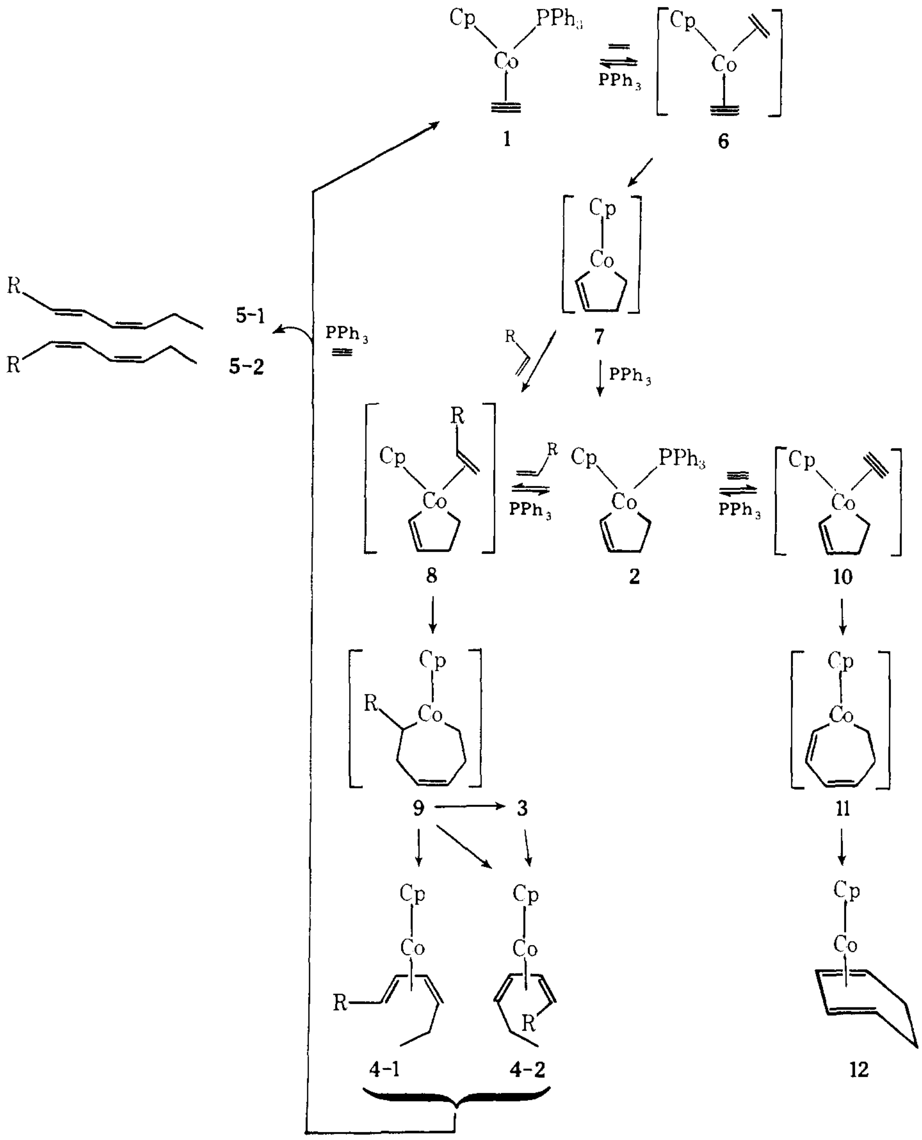
Reaction of 2a with an Olefin. Complex **2a** reacted with acrylonitrile at room temperature to give a diene complex with an empirical formula $Co(C_5H_5)(PhC_2CO_2Me)(MeO_2CCH)_2(CH_2CHCN)$ (**4a-1**) and a complex formulated as $Co(C_5H_5)(PhC_2CO_2Me)(MeO_2CCH)_2(CH_2CHCN)(PPh_3)$ (**3a**). The structure of **3a** has been established by an X-ray analysis to be a η^2-diene complex in which the cobalt is coordinated by a cis-olefinic fragment originating from acrylonitrile (Figure 4).[12] On heating a benzene solution of **3a** at 70 °C, PPh_3 was eliminated and a η^4-diene complex (**4a-2**), an isomer of **4a-1**, was formed. Based on a reasonable assumption that the configuration of the diene was maintained but the conformation changed from s-trans to s-cis during the thermal transformation of **3a** to **4a-2**, the structure of **4a-2** has been assigned as illustrated in Figure 4. Through this process, then, the configuration of cobalt is expected to undergo inversion.

The molecular geometry of **4a-1** shown in Figure 4 has also been determined by a single-crystal X-ray analysis.[13] Based on these structural analyses, the reaction scheme could be speculated in some more detail. In particular, it was possible to see whether the configuration of cobalt changed, because these complexes, as well as the starting cobaltacyclopentene (**2a**), have an asymmetric carbon the configuration of which should not change during the reactions.

The first step in the reaction of **2a** with acrylonitrile may be the displacement of the phosphine ligand with the olefin, a reaction path which will be suggested later for similar reaction of acetylene (based on kinetic study). By analogy with the case of acetylene, the configuration of cobalt may be retained in this process also, i.e., the acrylonitrile molecule attacks the same coordination site which has been occupied by the phosphine.

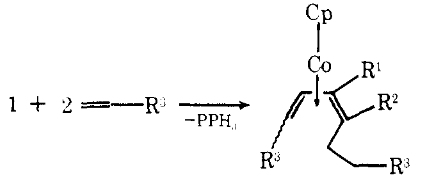
We propose the next step involving regio- and stereospecific insertion of the coordinated olefin into the Co-vinylic carbon σ bond, forming a coordinatively unsaturated seven-membered cobalt metallocycle in such a way that the nitrile group is oriented away from the two CO_2Me groups (originated from dimethyl maleate) to avoid steric interactions (Figure 5). Before the β-hydrogen transfers, the cobaltacycloheptene (**9-1**) thus formed would attain an equilibrium with its diastereomeric isomer (**9-2**).[14] It is reasonable to assume that the next step, involving β-hydride transfer and reductive alkyl elimination, takes place through a conformation in which Co-C-C-H_{cis} is almost coplanar;[15] such conformations for each isomer are illustrated in Figure 5. The formation of η^4-diene complex **4a-1** is easily rationalized using the hypothesis that it is formed from **9-1** and the β-hydride-alkyl-elimination

Scheme I



process is accompanied by an attack of the double bond onto the uncoordinated position; this is indicated by the broken arrow in Figure 5 (**9-1**). This thus leads to an inversion of the cobalt configuration. The elimination of β-hydride-alkyl of **9-2**, in which such attack of the double bond on the uncoordinated position is hindered by the two bulky R's (CO_2Me), will result in mere formation of the η^2-diene complex with retention of the configuration at cobalt atom. The vacant coordination site will be occupied again with PPh_3 to give **3a**.

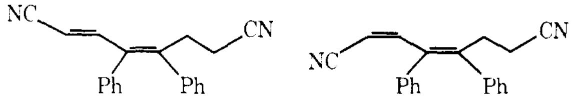
As described before, **4a-2** was formed on heating **3a** at 70 °C. Therefore the reaction of **2a** with acrylonitrile, when carried out at 70 °C, should give directly **4a-2** together with **4a-1**; this was confirmed to be the case. Analogous diene complexes were obtained by the reaction of **1a** or **1b** with monosubstituted olefins (eq 6). It is clear that **4b** and **4c** were formed via a cobaltacyclopentene intermediate similar to **2a–e**. In the latter two reactions, which were carried out at room temperature, only one isomer was obtained. Seemingly, one of the two stereoisomers in the seven-membered cobaltacycle **9** predominates over the other in these cases.



(6)

4b, R^1 = Ph; R^2 = CO_2Me; R^3 = CN
4c, R^1 = R^2 = R^3 = CO_2Me

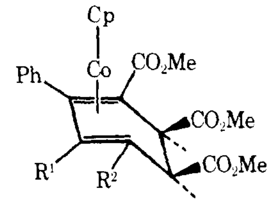
If the diene ligand in the η^4-diene complex **4** is replaced with acetylene, the system will provide a catalytic cycle. This was realized in the case of diphenylacetylene–acrylonitrile. Thus when diphenylacetylene and acrylonitrile were heated at 70 °C in the presence of a catalytic amount of **1c**, **5a-1** and **5a-2** were obtained as colorless crystals in ca. 1:1 ratio. The coupling constants of the two diene protons of **5a-1** and **5a-2** were 16 and 11 Hz, respectively.



5a-1 **5a-2**

On the grounds of the discussion above, the reaction sequences for the catalytic cycle are depicted in Scheme I.

Reaction of 2a with Acetylenes. Complex **2a** reacted with methyl phenylpropiolate at room temperature to give a cyclohexadiene complex (**12a**) which has been prepared previously by another route, i.e., the reaction of a cobaltacyclopentadiene with dimethyl maleate.[8a] The formation of a similar cyclohexadiene complex (**12b**), by the reaction of **2a** with diphenylacetylene, was monitored by NMR spectroscopy. The



12a, $R^1 = CO_2Me$; $R^2 = Ph$
12b, $R^1 = R^2 = Ph$

observed reaction rate could be accommodated by the mechanism

$$\mathbf{2a} + \text{Ph-}\!\equiv\!\text{-Ph} \overset{K}{\rightleftarrows} \mathbf{10b} + \mathrm{PPh_3} \tag{7}$$

$$\mathbf{10b} \xrightarrow{k_2} \mathbf{12b} \tag{8}$$

where **10b** is the cobaltacyclopentene coordinated by diphenylacetylene. As expected from eq 7, free triphenylphosphine added to the initial reaction mixture markedly hindered the reaction. For example, when a sixfold excess of diphenylacetylene was reacted with **2a** for 100 h with initial PPh_3 concentrations of 0, 0.5, and 1 M (based on **2a**), the conversions were 30, 11, and 5%, respectively. Figure 6 shows that the observed kinetic data could be satisfactorily described by the expression

$$\frac{d(\mathbf{12b})}{dt} = k_2K\,\frac{(a - \mathbf{12b})(b - \mathbf{12b})}{(\mathbf{12b}) + (c)},\ k_2K = 2.8 \times 10^{-8}\ \mathrm{s}^{-1} \tag{9}$$

where (a), (b), and (c) are the initial concentrations of **2a**, diphenylacetylene, and triphenylphosphine.

For **10** to **12** transformation, we suggest again a seven-membered cobalt metallocycle (**11**) as an intermediate (see Scheme I).[16] Further, by comparing the structure of **12a** with that of **2a**, we conclude that the configuration of cobalt was retained during the reaction.

Our observations presented here, together with that reported by Green et al.,[9] suggest that metallocyclopentene (II), as well as metallocyclopentadiene (I), could be an intermediate for the catalytic 2:1 cocyclotrimerization of alkyne with alkene.

Molecular Structure of 2a. Atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms, derived from the final cycle of least-squares refinement, are given in Table II. Bond lengths and angles are listed with their standard deviations in Tables III and IV, respectively. The perspective ORTEP drawing of Figure 1 illustrates the numbering scheme used for nonhydrogen atoms.

The molecular geometry may be compared with those of cyclopentadienyl(triphenylphosphine)tetrakis(pentafluorophenyl)cobaltacyclopentadiene (**13**)[17] and cyclopentadienyl(triphenylphosphine)cobaltacyclopentane (**14**).[18] Although the geometry around the cobalt atoms in these three related complexes is essentially the same, the geometries of the metallocycles, as expected, are quite different from each other. The C(1) to C(4) fragment of the cobaltacyclopentadiene **13** is planar with small displacement of the cobalt atom toward the Cp ring. In cobaltacyclopentane **14**, the atomic sequence Co-C(1)-C(3)-C(4) forms a plane with C(2) tipped away from this plane in the direction of the Cp ring. In **2a**, however, it is Co-C(1)-C(2)-C(3) that forms a plane and C(4) is displaced by 0.583 Å from the plane away from the Cp ring. The dihedral angle between Co-C(1)-C(2)-C(3) and Co-C(4)-C(3) is 34.2°. The Co-sp^2 carbon C(1) distance of 1.947 (11) Å is somewhat shorter than those in **13** (1.995 (11) and 1.993 (11) Å), whereas the Co-sp^3 carbon C(4) distance of 2.097 (12) Å in **2a** is longer than the corresponding values in **14** (2.025 (6) and 2.024 (7) Å).

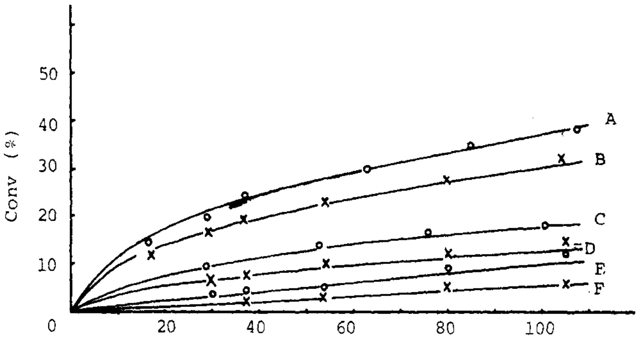


Figure 6. The rate of cyclohexadiene complex (**12b**) formation from **2a**, 0.6×10^{-4} M, and diphenylacetylene: (A) PhC_2Ph, 6.0×10^{-4} M; (B) PhC_2Ph, 3.6×10^{-4} M; (C) PhC_2Ph, 1.2×10^{-4} M; (D) PhC_2Ph, 0.6×10^{-4} M; (E) PhC_2Ph, 3.6×10^{-4} M; PPh_3, 0.3×10^{-4} M; (F) PhC_2Ph, 3.6×10^{-4} M; PPh_3, 0.6×10^{-4} M. The normal lines show theoretical curves calculated using eq 9.

Experimental Section

All the reactions were carried out under an atmosphere of nitrogen.

Materials. Olefins and acetylenes were commercial grade and used without further purification. Acetylene complexes of cobalt (**1a–c**) were prepared according to the previously reported method.[7] Sumitomo activated alumina KCG-30 and Wako-gel C-200 were used for column chromatography.

Preparation of Cobaltacyclopentenes. Cobaltacyclopentene complexes were prepared simply by adding appropriate olefin at room temperature to a benzene solution of an acetylene complex.

Dimethyl maleate (2 mL) was added to a benzene solution (30 mL) of **1a** (500 mg, 0.92 mmol). After 2 days at room temperature the brown-red solution was concentrated under a reduced pressure and the residue was chromatographed on alumina (2.5 × 13 cm). A brown band and a red band separated. From the brown band, which was eluted with benzene, a small amount of unreacted **1a** was recovered. The red band was eluted slowly with CH_2Cl_2 to remove a small amount of yellow-brown contaminant which came out just before the main red fraction. Removal of the solvent from the eluate and crystallization from benzene-hexane gave brown-red crystals of **2a** (191 mg): IR (KBr) 3050, 2980, 2930, 2860, 2820, 1725, 1690, 1665, 1565, 1480, 1430, 1315, 1290, 1238, 1188, 1163, 1140, 1085, 818, 795, 690, 520, 510, 500 cm^{-1}.

Crotononitrile (0.5 mL) was added to **1a** (395 mg, 0.72 mmol) in benzene (10 mL) and after 5 days the mixture was chromatographed on alumina (1.5 × 6 cm). From the dark-brown fraction which was eluted with benzene/CH_2Cl_2 (2/1), unreacted **1a** (143 mg) was recovered. The red-orange band was eluted with benzene/THF (20/1) from which dark-red crystals of **2b** (34 mg) were obtained on crystallization from hexane. The NMR spectrum showed this to be a 4:1 mixture of two isomers: IR (KBr) 3070, 2960, 2870, 2200, 1685, 1490, 1435, 1300, 1235, 1090, 870, 843, 818, 748, 699, 525, 510 cm^{-1}.

Dimethyl maleate (0.5 mL) was added to a solution of **1b** (132 mg, 0.25 mmol) in benzene (15 mL) and the mixture was allowed to stand at room temperature for 2 days. After concentration under a reduced pressure, the residue was chromatographed on alumina (1.5 × 8 cm). The orange band was eluted with CH_2Cl_2/THF (10/1). The volume of the eluate was reduced (ca. 1 mL) and hexane (5 mL) added to give red crystals of **2c** (108 mg): IR (KBr) 3080, 3020, 2970, 1728, 1712 (s), 1702, 1578, 1490, 1440, 1432, 1320, 1230, 1215, 1172, 1160, 1093, 1045, 1008, 998, 818, 755, 700, 535, 510, 505 (s) cm^{-1}.

Dimethyl fumarate (300 mg) and **1b** (132 mg, 0.25 mmol) in benzene (15 mL) were allowed to stand for 2 days. The reaction mixture was concentrated and chromatographed on alumina (2 × 12 cm). Elution with CH_2Cl_2 gave a small amount of purple-brown fraction from which **1b** (10 mg) was recovered. Further elution with CH_2Cl_2/THF (5/1) gave two orange bands which separated clearly. Removal of the solvent from the first orange fraction gave red oil (18 mg) of **2dT-2** which did not crystallized after 4 days in hexane. From the second orange fraction, dark-red crystals of **2dT-1** were obtained on concentration and addition of hexane: IR (KBr) 3120, 3080, 3010,

Table II. Atomic Coordinates and Thermal Parameters in **2a**[a]

atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	1140 (2)	2349 (1)	370 (2)	76	30	165	2	66	−6
P	3038 (2)	1929 (1)	2056 (3)	56	20	121	2	46	−5
C(1)	1527 (8)	3251 (5)	−219 (13)	48	16	154	0	41	−8
C(2)	1288 (9)	3254 (5)	−1870 (13)	53	21	153	3	51	−7
C(3)	866 (8)	2525 (6)	−2972 (12)	44	26	119	3	34	−3
C(4)	1224 (9)	1885 (6)	−1846 (13)	70	26	125	4	63	−12
C(5)	1273 (9)	3867 (6)	−2758 (14)	62	30	171	7	62	−3
C(6)	1542 (15)	5164 (7)	−2757 (20)	176	28	308	−11	117	6
C(7)	−485 (10)	2654 (6)	−4124 (13)	70	32	125	−1	41	−11
C(8)	−1984 (12)	2403 (11)	−6871 (17)	66	99	154	−4	18	−28
C(9)	591 (10)	1193 (6)	−2559 (13)	85	30	133	4	76	−15
C(10)	799 (12)	−165 (6)	−2572 (17)	114	23	238	−7	74	−10
C(11)	1953 (10)	3903 (6)	986 (14)	80	19	155	4	54	−13
C(12)	1143 (11)	4436 (6)	1429 (16)	98	24	221	5	79	−22
C(13)	1583 (14)	5054 (7)	2602 (19)	150	31	314	−7	143	−43
C(14)	2805 (14)	5169 (7)	3372 (18)	145	32	234	−8	77	−25
C(15)	3631 (13)	4646 (7)	2951 (19)	109	29	296	−13	57	−28
C(16)	3194 (11)	4025 (7)	1771 (17)	76	29	266	−6	52	−27
C(21)	3914 (9)	2552 (6)	3862 (13)	70	24	143	−5	55	−14
C(22)	3314 (11)	3030 (7)	4720 (15)	97	38	164	−3	71	−30
C(23)	3998 (12)	3477 (8)	6179 (17)	93	45	215	−7	70	−34
C(24)	5253 (13)	3453 (8)	6766 (18)	107	43	253	−16	66	−38
C(25)	5822 (12)	2984 (8)	5894 (17)	95	48	210	−14	72	−34
C(26)	5175 (10)	2528 (7)	4485 (15)	65	38	193	−6	54	−24
C(31)	4128 (9)	1642 (6)	1111 (12)	58	26	119	−1	41	−13
C(32)	4900 (10)	948 (6)	1521 (15)	68	31	186	5	62	−5
C(33)	5766 (11)	787 (7)	822 (16)	80	34	239	6	80	−18
C(34)	5845 (11)	1250 (7)	−155 (16)	87	38	203	−4	80	−15
C(35)	5076 (11)	1939 (7)	−580 (15)	80	40	181	−7	69	−12
C(36)	4207 (9)	2118 (6)	96 (14)	59	30	169	−3	51	0
C(41)	3088 (9)	1098 (6)	3068 (13)	59	26	160	4	56	0
C(42)	2601 (10)	436 (6)	2067 (16)	76	23	247	1	71	−6
C(43)	2500 (11)	−178 (7)	2769 (16)	90	35	217	−3	72	0
C(44)	2879 (12)	−155 (7)	4484 (18)	100	38	259	−1	76	18
C(45)	3359 (14)	492 (8)	5467 (19)	132	37	258	−5	87	13
C(46)	3484 (12)	1112 (7)	4802 (15)	106	37	157	4	57	17
C(51)	−22 (10)	1648 (7)	569 (15)	73	36	208	−4	94	1
C(52)	−718 (9)	2163 (7)	−667 (16)	56	36	233	−4	84	−5
C(53)	−566 (9)	2933 (7)	94 (14)	54	40	161	3	66	−20
C(54)	214 (9)	2881 (7)	1841 (14)	63	41	167	2	78	−12
C(55)	550 (9)	2084 (7)	2127 (14)	62	41	161	0	81	8
O(1)	911 (8)	3822 (5)	−4280 (10)	142	40	155	−1	84	2
O(2)	1625 (8)	4525 (4)	−1880 (11)	127	29	202	−11	75	−2
O(3)	−1245 (7)	3016 (5)	−3717 (10)	63	47	176	14	55	−18
O(4)	−729 (7)	2331 (5)	−5666 (9)	74	55	109	−4	46	−19
O(5)	−459 (7)	1163 (4)	−3574 (10)	74	32	191	−6	40	−18
O(6)	1331 (7)	543 (4)	−1995 (10)	93	22	186	4	70	−6
Cl(1)	4926 (14)	4753 (9)	406 (19)	72 000					
Cl(2)	5735 (13)	3924 (8)	987 (18)	63 300					

[a] The values have been multiplied by 10^4. The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

2960, 2850, 1733, 1708, 1698, 1588, 1488, 1435, 1260, 1225, 1200, 1135, 1090, 1040, 1015, 1008, 997, 822, 750, 700, 645, 523, 511, 500 cm^{-1}.

Fumaronitrile (40 mg) and **1b** (132 mg, 0.25 mmol) were dissolved in benzene (15 mL). After 6 days at room temperature, the mixture was chromatographed on alumina (2 × 5 cm). A yellow band was eluted with benzene/THF (10/1). Concentration of the eluate and addition of hexane gave brown-red crystals of **2e** (28 mg) which were a 2:3 mixture of the two isomers: IR (KBr) 3130, 3080, 2960, 2850, 2200, 1706, 1578, 1485, 1438, 1390, 1268, 1220, 1195, 1138, 1090, 1040, 998, 848, 830, 750, 699, 682, 528, 511, 492 cm^{-1}.

Reaction of Cobaltacyclopentene with Acrylonitrile. Acrylonitrile (5 mL) was added to a benzene (30 mL) solution of **2a** (340 mg, 0.49 mmol). After 3 days at room temperature, the solution was chromatographed on alumina (1.5 × 13 cm). A dark-brown band, a purple-brown band, and an orange-brown band separated. From the first dark-brown band, which was eluted with benzene/THF (20/1), brown powder was obtained on concentration in vacuo. This powder was recrystallized from CH_2Cl_2/hexane to give dark-red crystals of **3a** (108 mg, solvated with CH_2Cl_2, 27% yield): mp 154 °C dec; ^1H NMR ($CDCl_3$) δ 5.28 (CH_2Cl_2), 4.58 (s, C_5H_5), 3.91, 3.78, and 3.24 (s, CO_2CH_3), 1.78 and 1.00 (t, $J_{PH} = J_{HH} = 8$ Hz, olefinic H), 5.33 (q, $J_{HH} = 4$ and 12 Hz, aliphatic H), 2.91 (q, $J_{HH} = 12$ and 17 Hz, aliphatic H), 1.98 (q, $J_{HH} = 4$ and 17 Hz, aliphatic H); IR (KBr) 3020, 2970, 2200, 1735, 1480, 1435, 1310, 1240, 1160, 1088, 1010, 990, 832, 815, 745, 695, 530, 512, 488 cm^{-1}. Anal. Calcd for $C_{43}H_{41}Cl_2NO_6PCo$: C, 62.33; H, 4.99; N, 1.69. Found: C, 62.51; H, 5.00; N, 1.71. The second purple-brown band was eluted with benzene/THF (20/1) and the volume was reduced. The residue was crystallized from benzene/hexane to give dark-red crystals of **4a-1** which was further purified by recrystallization from CH_2Cl_2/hexane (27 mg, solvated with ½ CH_2Cl_2, 11% yield): mp 120-123 °C dec; ^1H NMR ($CDCl_3$) δ 5.70 (d, $J = 9$ Hz, H), 5.28 (CH_2Cl_2), 4.96 (s, C_5H_5), 3.79, 3.63, and 3.44 (s, CO_2CH_3), 3.1-3.4 and 2.2-2.5 (m, H), 1.78 (d, $J = 9$ Hz, H); IR (KBr) 3050, 2980, 2930, 2820, 2200, 1720, 1663, 1425, 1280, 1242, 1195, 1150, 1108, 1078, 1000, 898, 853, 815, 780, 758, 699, 660 cm^{-1}. Anal. Calcd for $C_{24.5}H_{25}ClNO_6Co$: C, 56.17; H, 4.81; N, 2.67; mol wt, 481.4. Found: C, 55.75; H, 4.80; N, 2.54; mol wt, 481 (mass spectrum). From the third orange-brown band unreacted **2a** was recovered (28 mg). When this reaction was performed at 70 °C for 7 h and the reaction mixture was treated on alumina chromatography, **4a-1** (15% yield) and **4a-2** (2.5% yield) were obtained; no fraction for **3a** nor **2a** was observed.

Thermal Elimination of PPh_3 from 3a. A benzene (10 mL) solution of **3a** (80 mg, 0.0965 mmol) was heated at 70 °C. After 7 h the resulting dark-red solution was concentrated in vacuo. Column chromatography (alumina, 1.5 × 12 cm) of the residue gave a brown-red band. Removal of the solvent (benzene/THF (10/1)) from the eluate followed by crystallization from hexane yielded dark-red crystals of **4a-2** (12 mg, 26% yield): mp 181-182 °C dec; ^1H NMR ($CDCl_3$) δ 5.77 (d, *J* = 8 Hz, H), 4.94 (s, C_5H_5), 3.75, 3.66, and 3.42 (s, CO_2CH_3), 2.8-3.1 and 1.1-1.2 (m, H), 1.23 (d, *J* = 8 Hz, H); IR (KBr) 3010, 2970, 2860, 2210, 1720, 1678, 1435, 1360, 1305, 1250, 1218, 1180 (s), 1125, 1085, 1040, 1000, 925, 848, 832, 817, 790, 780, 752, 700, 680 cm^{-1}. Anal. Calcd for $C_{24}H_{24}NO_6Co$: C, 59.90; H, 5.03; N, 2.91; mol wt, 481.4. Found: C, 59.41; H, 4.99; N, 2.92; mol wt, 481 (mass spectrum).

Reaction of Acetylene Complex 1 with Acrylic Compounds. A mixture of **1a** (160 mg, 0.29 mmol) and acrylonitrile (1 mL) in benzene (10 mL) was allowed to stand overnight at room temperature. Chromatographic workup (silica gel, 1.5 × 15 cm) of the concentrated solution gave a brown-red band which was eluted with benzene/ CH_2Cl_2 (1/1). Concentration of the eluate in vacuo and addition of hexane afforded dark-red crystals of **4b** (18 mg, 16% yield): mp 155-157 °C dec; ^1H NMR ($CDCl_3$) δ 5.70 (d, *J* = 8 Hz, H), 4.98 (s, C_5H_5), 3.40 (s, CO_2CH_3), 2.3-2.8 and 1.5-1.7 (m, H), 0.78 (d, *J* = 8 Hz, H); IR (KBr) 3140, 3050, 2990, 2960, 2250, 2220, 1673, 1503, 1465, 1453, 1433, 1325, 1248, 1190, 1175, 1129, 1094, 822, 752, 700, 673, 625, 570 cm^{-1}. Anal. Calcd for $C_{21}H_{19}N_2O_2Co$: C, 64.62; H, 4.91; N, 7.18. Found: C, 65.12; H, 4.83; N, 7.19.

By a similar treatment of **1b** with methyl acrylate, dark-red crystals of **4c** were obtained (58% yield): mp 112-114 °C dec; ^1H NMR ($CDCl_3$) δ 6.33 (d, *J* = 9 Hz, H), 4.74 (s, C_5H_5), 3.85, 3.72, 3.67, and 3.64 (s, CO_2CH_3), 2.3-2.7, 0.9-1.3, and 0.4-0.7 (m, H), 1.63 (d, *J* = 9 Hz, H); IR (KBr) 3025, 2970, 2870, 1738, 1700, 1440, 1242, 1199, 1172 cm^{-1}. Anal. Calcd for $C_{19}H_{23}O_8Co$: C, 52.06; H, 5.29; mol wt, 438.3. Found: C, 52.21; H, 5.28; mol wt, 438 (mass spectrum).

Catalytic Reactions. A mixture of **1c** (57 mg, 0.1 mmol), diphenylacetylene (712 mg, 4 mmol), acrylonitrile (7 mL), and benzene (7 mL) was heated at 70 °C for 5 days. The concentrated reaction mixture was chromatographed on alumina (1.5 × 18 cm). A benzene fraction (200 mL) was discarded and two colorless fractions eluted with CH_2Cl_2 (100 mL each) were collected. The solvent was then evaporated and the residue was crystallized from cold hexane. From the first fraction, a mixture of **5a-1** and **5a-2** (total 109 mg) was obtained and they were separated by another chromatographic workup to give pure **5a-1** (25 mg) and **5a-2** (53 mg). The second fraction afforded pure **5a-1** (35 mg). **5a-1**: mp 101-102 °C; ^1H NMR ($CDCl_3$) δ 7.82 (d, *J* = 16 Hz, olefinic H), 5.09 (d, olefinic H), 3.14 (t, *J* = 7 Hz, aliphatic H), 2.40 (t, aliphatic H); IR (KBr) 3060, 3020, 2940, 2230, 2200, 1595, 1488, 1460, 1440, 1420, 1328, 1068, 1025, 965, 915, 825, 778, 720, 698, 643, 610, 525 cm^{-1}. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.45; H, 5.67; N, 9.85. Found: C, 84.57; H, 5.76; N, 10.02. **5a-2**: mp 126-128 °C; ^1H NMR ($CDCl_3$) δ 7.39 (d, *J* = 11 Hz, olefinic H), 5.54 (d, olefinic H), 3.08 (t, *J* = 7 Hz, aliphatic H), 2.38 (t, aliphatic H); IR (KBr) almost identical with that of **5a-1** except for the absence of the 965-cm^{-1} band. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.45; H, 5.67; N, 9.85; mol wt, 284.4. Found: C, 84.66; H, 5.62; N, 10.17; mol wt, 284 (mass spectrum).

Reaction of 2a with Acetylenes. To a solution of **2a** (150 mg, 0.22 mmol) in benzene (10 mL) was added methyl phenylpropiolate (0.5 mL). After 3 days at room temperature column chromatography on alumina (1.5 × 13 cm) gave an orange-yellow band which was eluted with CH_2Cl_2. After the removal of solvent the residue was crystallized from hexane to afford brown-red crystals of **12a** (62 mg, 43% yield), which has been previously obtained by another method.[8a] By a similar reaction and procedure using **2a** and diphenylacetylene, dark-red crystals of **12b** were obtained in 46% yield: mp 204-206 °C dec; ^1H NMR ($CDCl_3$) δ 5.28 (s, C_5H_5), 3.64, 3.24, and 3.14 (s, CO_2CH_3), 2.70 (AB q, J_{AB} = 9 Hz, $\delta_A - \delta_B$ = 0.45 ppm); IR (KBr) 3080, 3040, 3020, 2980, 2940, 2870, 2825, 1743, 1732, 1692, 1490, 1428, 1280, 1185, 1170, 1148, 1130, 810, 740, 698 cm^{-1}. Anal. Calcd for $C_{35}H_{31}O_6Co$: C, 69.31; H, 5.15. Found: C, 69.72; H, 5.13.

Table III. Selected Bond Distances (Å) in **2a**

atoms	distance	atoms	distance
Co-P	2.232 (3)	C(2)-C(5)	1.433 (17)
Co-C(1)	1.947 (11)	C(5)-O(1)	1.228 (15)
Co-C(4)	2.079 (12)	C(5)-O(2)	1.334 (13)
Co-C(51)	2.119 (14)	O(2)-C(6)	1.439 (19)
Co-C(52)	2.120 (11)		
Co-C(53)	2.124 (11)	C(3)-C(7)	1.526 (13)
Co-C(54)	2.140 (14)	C(7)-O(3)	1.214 (15)
Co-C(55)	2.134 (15)	C(7)-O(4)	1.338 (13)
		O(4)-C(8)	1.444 (13)
C(1)-C(2)	1.375 (17)		
C(2)-C(3)	1.527 (13)	C(4)-C(9)	1.475 (15)
C(3)-C(4)	1.513 (15)	C(9)-O(5)	1.214 (12)
		C(9)-O(6)	1.365 (12)
C(1)-C(11)	1.459 (13)	O(6)-C(10)	1.437 (14)
C(11)-C(12)	1.417 (18)		
C(12)-C(13)	1.402 (17)	C(51)-C(52)	1.419 (16)
C(13)-C(14)	1.388 (22)	C(52)-C(53)	1.445 (16)
C(14)-C(15)	1.412 (22)	C(53)-C(54)	1.438 (14)
C(15)-C(16)	1.410 (17)	C(54)-C(55)	1.444 (16)
C(16)-C(11)	1.411 (16)	C(55)-C(51)	1.430 (15)
		P-C(21)	1.827 (10)
		P-C(31)	1.858 (13)
		P-C(41)	1.823 (12)

Table IV. Selected Bond Angles (deg) in **2a**

atoms	angle	atoms	angle
C(1)-Co-C(4)	82.0 (4)	C(2)-C(3)-C(4)	108.0 (9)
C(1)-Co-P	97.0 (3)	C(2)-C(3)-C(7)	109.7 (9)
C(4)-Co-P	96.2 (3)	C(4)-C(3)-C(7)	115.4 (9)
		Co-C(4)-C(3)	107.5 (7)
Co-C(1)-C(2)	115.6 (8)	Co-C(4)-C(9)	113.3 (8)
Co-C(1)-C(11)	122.0 (8)	C(3)-C(4)-C(9)	117.1 (9)
C(2)-C(1)-C(11)	122.3 (9)		
C(1)-C(2)-C(3)	116.1 (9)	Co-P-C(21)	118.8 (4)
C(1)-C(2)-C(5)	129.4 (10)	Co-P-C(31)	117.4 (4)
C(3)-C(2)-C(5)	114.2 (9)	Co-P-C(41)	111.9 (4)

Kinetics. The kinetic study on the formation of cobaltacyclopentene complex was conducted at 24.2 °C in C_6D_6 solutions. A mixture of **1b** (26.5 mg, 0.05 mmol) and triphenylphosphine (four runs: 0, 6.55, 13.0, and 19.65 mg; 0, 0.025, 0.05, and 0.075 mmol, respectively) was placed in a NMR tube and dissolved in C_6D_6 (0.5 mL) containing dimethyl maleate (72 mg, 0.5 mmol). The reaction was followed by peak intensities of sharp cyclopentadienyl resonances of **1b** (δ 4.66 ppm) and **2c** (5.00 ppm).

The reaction of **2a** with diphenylacetylene was also followed by monitoring the intensity change of the cyclopentadienyl resonances, in $CDCl_3$ at 24.2 °C. Four runs were performed with a constant initial concentration of **2a** (41.4 mg, 0.06 mmol, in 0.2 mL of $CDCl_3$) and various concentrations of diphenylacetylene (0.6, 0.36, 0.12, and 0.06 mmol). Further, two runs with initial addition of PPh_3 (0.06 and 0.03 mmol) to the system **2a**/PhC_2Ph (0.06/0.36) were examined.

X-ray Study of 2a. Crystals suitable for an X-ray analysis were grown from a CH_2Cl_2/hexane solution. The crystal used was an irregularly shaped columnar with dimensions 0.5 × 0.4 × 0.4 mm. Preliminary Weissenberg photographs showed neither systematic absence nor diffraction symmetry higher than *Ci*($\bar{1}$). The crystal was, therefore, assumed to be triclinic, space group *P*1 or *P*$\bar{1}$. The successful solution and subsequent refinement of the structure confirms the choice of the centrosymmetric space group *P*$\bar{1}$.

The unit cell constants of *a* = 12.330 (5) Å, *b* = 17.834 (6) Å, *c* = 8.955 (4) Å, α = 98.123 (3)°, β = 116.134 (3)°, γ = 81.128 (3)° were determined from high-order reflections on a Rigaku four-circle automatic diffractometer. The unit cell volume is 1740.7 Å^3, yielding a calculated density of 1.359 g cm^{-3} for $CoPO_6C_{39}H_{36}\cdot\frac{1}{4}CH_2Cl_2$ (mol wt 711.858) and *Z* = 2. The experimental density as determined by flotation in an aqueous solution of KI was found to be 1.36 (3) g cm^{-3}. The crystal was mounted such that the axis was nearly parallel to the ϕ axis of the diffractometer. The intensity data were collected by the 2θ-ω scan method using Cu Kα radiation monochromated by 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 eacn scan. Three standard reflections were monitored before every 52 measurements. A total of 6344 independent intensities in the range $2\theta \leq 133°$ were measured. The treatment of the intensity data has been previously described.[19] The 4674 reflections for which $F_o > 3\sigma(F_o)$ were used in the solution and refinement of the structure. The intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient of the compound for Cu Kα was 54.87 cm^{-1}. Although the crystal was longer than optimum size, no absorption correction was applied because the crystal was irregularly shaped and had no well-defined face. It is therefore probable that the values of the anisotropic thermal parameters reflect to some extent our neglect of absorption.

The coordinates of the cobalt and phosphorus atoms were determined from a sharpened Patterson map. The subsequent structure factor and electron density map calculations revealed the positions of other atoms except crystallized solvent (CH_2Cl_2). Five cycles of a 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 $R_2 = [\Sigma w(|F_o| - |F_c|)^2/wF_o^2]^{1/2}$ of 17.3 and 20.0% (using unit (equal) weight), respectively. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$. Five cycles of further refinement with anisotropic thermal parameters converged to $R_1 = 13.5\%$ and $R_2 = 16.9\%$. At this stage, an electron density difference map was calculated to locate the crystallized solvent; it showed two broad peaks smaller than 4 e/Å^3 in a gap of the crystal lattice, suggesting high disorder of the CH_2Cl_2 group. Four more cycles of refinement including two $^1/_4$ weighted Cl atoms with isotropic thermal parameters converged to lower residual factors $R_1 = 10.2\%$ and $R_2 = 12.3\%$. In these refinements, the weighting scheme was of the type suggested by Hughes,[20] where $\sqrt{w} = 1.0$ for $F_o \leq 3$ and $\sqrt{w} = 3/F_o$ for $F_o > 30$. No unusual trends were observed in the analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of either $\sin\theta/\lambda$ or $|F_o|$ In the final cycle of the refinement, no positional parameter exhibited shifts of more than 0.3 times its estimated standard deviation. Anomalous dispersion effects of Co were included in the calculation of F_c using $\Delta f'$ and $\Delta f''$ calculated by Cromer.[21] The atomic scattering factors were the usual tabulation.[22] The computer programs used are listed elsewhere.[19] A list of the observed and the calculated structure factor amplitudes is available.[23]

Supplementary Material Available: A listing of the observed and the calculated structure amplitudes for **2a** (14 pages). Ordering information is given on any current masthead page.

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(12) Crystals of **3a** were of relatively poor quality for a diffraction study. To date we have been unsuccessful in obtaining accurate atomic coordinates, although overall molecular geometry is quite reasonable. *R* currently stands at 0.15. Crystal data: orthorhombic, $a = 18.067$ (5) Å, $b = 22.612$ (6) Å, $c = 17.719$ (5) Å, $V = 7238.8$ Å^3, $Z = 8$, mol wt 743.7, space group *Pbca*. Crystals used for the diffraction study were obtained from $CHCl_3$/hexane solution.

(13) The detailed results of this crystal analysis will be published elsewhere with that of other $Co(C_5H_5)$ (diene) complexes.

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