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COBALT METALLOCYCLES

III *. THERMOLYSIS OF COBALTACYCLOPENTADIENE COMPLEXES

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Summary

Thermolysis of (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes has been found to give (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt complexes in reasonable yields. Similar treatment of benzyl-substituted cyclopentadienyl derivatives gave diene complexes, $(\eta^5\text{-}C_5H_5CH_2\overline{C_6H_4)(\eta^4\text{-}C}R^1{=}CR^2CR^3{=}CHR^4)Co$, which were formed by addition of the *ortho* hydrogen of the benzyl group to the cobaltacyclopentadiene ring.

The simplest method of preparing cyclobutadiene complexes of transition metals is direct cycloaddition of two acetylene molecules to the metal.

There are several reports of the synthesis of (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt derivatives from acetylenes and cobalt complexes such as $(\eta^5\text{-}C_5H_5)_2Co$, $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Co$, and $(\eta^5\text{-}C_5H_5)(CO)_2Co$ [2]. According to this method, it is impossible to obtain a complex in which cyclobutadiene moiety is substituted with more than three different groups because the substituents are limited by the acetylene employed.

Previously, we have shown that thermolysis of a tetraphenylcobaltacyclopentadiene complex, $(\eta^5\text{-}C_5H_5)(PPh_3)(\overline{CoCPh{=}CPhCPh{=}CPh})$, yields the corresponding cyclobutadiene complex, $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4Ph_4)Co$ [3]. We have recently reported that a variety of substituents can be introduced on the cobaltacyclopentadiene ring by the stepwise reaction of two different acetylenes with $(\eta^5\text{-}C_5H_5)(PPh_3)_2Co$ [4]. In this reaction, introduction of a substituent on the cyclopentadienyl ring may also be achieved by using $(\eta^5\text{-}RC_5H_4)(PPh_3)_2Co$. By analogy with the tetraphenylcobaltacyclopentadiene complex, it was expected that the cobaltacyclopentadiene complexes thus obtained, $(\eta^5\text{-}RC_5H_4)(PPh_3)$-$(\overline{CoCR^1{=}CR^2CR^3{=}CR^4})$, would be converted to cyclobutadiene complexes by

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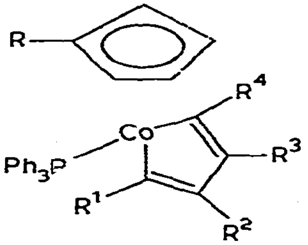
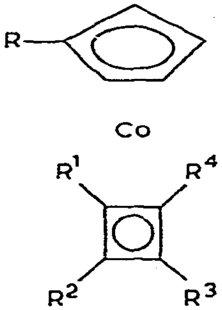
* Part II of this series, see ref. 1.

thermal release of the phosphine ligand, thus providing a general route to (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt complexes, in particular, those with different substituents. With this in mind, we have examined the thermolysis of the cobaltacyclopentadiene complexes bearing various substituents *.

Results and discussion

The thermolysis of (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes were carried out either by heating them just above their melting points for several minutes without solvent or by heating their solutions at 150°C for several hours. From unsubstituted cyclopentadienyl derivatives, yellow cyclobutadiene complexes were obtained in reasonable yields. They were very stable in air and exhibited very strong molecular ion peaks in their mass spectra.





A methylcyclopentadienyl derivative gave the corresponding cyclobutadiene complex. Unexpectedly, thermolysis of benzylcyclopentadienyl derivatives led to different products. When (η^5-benzylcyclopentadienyl)(triphenylphosphine)-tetraphenylcobaltacyclopentadiene (I) was heated above its melting point, a brick-red crystalline complex (IV) was obtained in addition to the cyclobutadiene complex, Furthermore, (η^5-benzylcyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene (II) and (η^5-benzylcyclopentadienyl)(triphenylphosphine)-2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene (III) gave only red-brown crystalline complexes, V and VI, without giving the cyclobutadiene complexes. Their molecular weights are identical with those of the corresponding cyclobutadiene complexes, as indicated by their mass spectra. In the NMR spectra of these complexes, the methylene protons of the benzyl group appeared as an AB type quartet. A sharp singlet corresponding to one proton was observed at high field. Based on these observations, it seemed plausible that a diene-type structure had been formed through ring opening of a cobaltacyclopentadiene by addition of a benzyl group. The structure of VI was confirmed by an X-ray crystallographic analysis [6]. The structure is described as [η^4-*syn*-*ortho*(η^5-cyclopentadienylmethyl)phenyl-1-*anti*-phenyl-2,3-dimethoxycarbonyl-4-*syn*-phenylbutadiene]cobalt.

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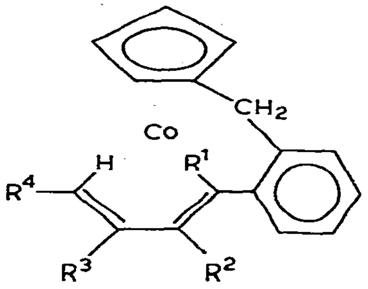
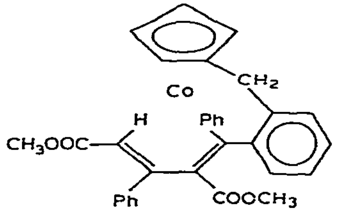
* Some related results were published separately [5].



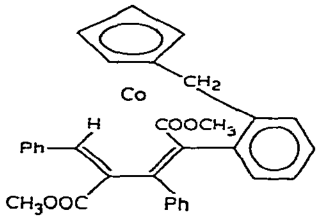
(IV) $R^1, R^2, R^3, R^4 = Ph$

(VI) $R^1, R^4 = Ph$; $R^2, R^3 = CO_2CH_3$

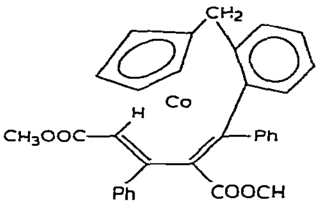
There are several possible structures, Va, Vb, and their *syn—anti* isomers such as Vc, for the red-brown solid V.



(Va)



(Vb)



(Vc)

In a separate experiment, we had obtained one of the possible isomers, Vc, whose structure was verified by an X-ray crystallographic analysis *. The compound Vc can be easily isomerized to V simply by heating just above the melting point for a few minutes. We suggest therefore, that solid V has the structure Va.

The physical properties of the cyclobutadiene complexes and butadiene complexes are summarized in Tables 2 and 3.

In the thermolysis of cobaltacyclopentadiene complexes, dissociation of triphenylphosphine may be the first step. Subsequent reductive coupling of Co—C bonds will result in the formation of cyclobutadiene complex. In the case of benzylcyclopentadienyl derivatives, the phenyl group of benzyl moiety may be in a suitable spatial arrangement for occupying a vacant coordination site of the cobalt. Thus, activation of the C—H bond and addition to the cobaltacyclopentadiene to give a butadiene complex may compete with cyclobutadiene complex formation (Scheme 1). Compound VI also has been isolated under mild conditions in the course of the synthesis of II and III, suggesting the intermediate formation of a coordinatively unsaturated cobaltacyclopentadiene complex prior to the formation of the desired complexes.

If the intermediate cobaltacyclopentadiene complex permits coordination of solvent benzene, an unsubstituted cyclopentadienyl derivative will also give

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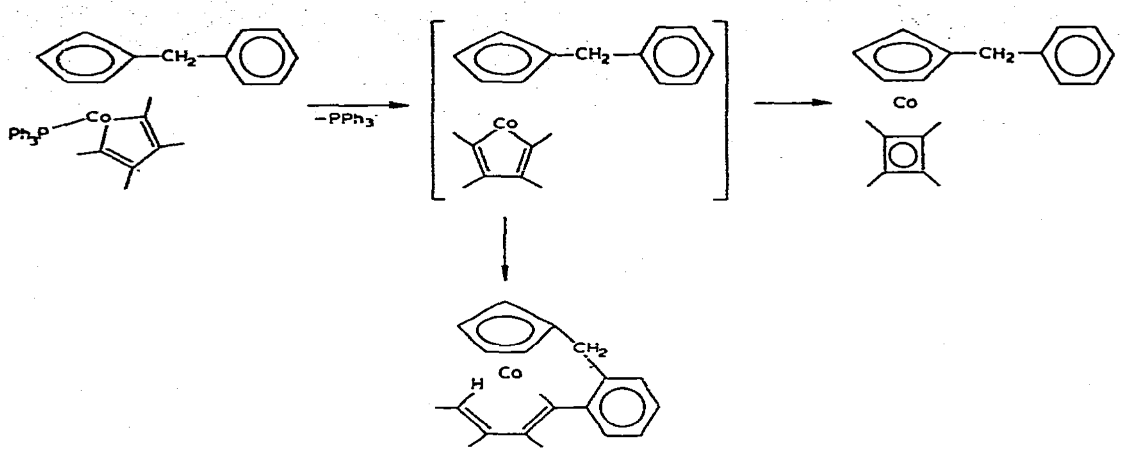
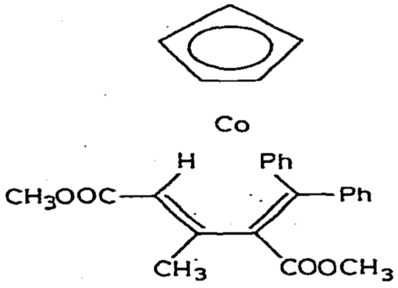
* One of the products of the reaction of (η^5-cyclopentadienyl)(triphenylphosphine)dibenzylcobalt with methyl phenylpropiolate. Black crystals; m.p. 169—171°C [6].

SCHEME 1



an open chain diene complex. We can assume a butadiene structure for the dark-red crystalline complex (VII) which was a minor product of thermolysis of (η^5-cyclopentadienyl)(triphenylphosphine)-2,4-dimethoxycarbonyl-3-methyl-5-phenylcobaltacyclopentadiene in benzene. In the present series of butadiene complexes, resonances of vinylic protons bonded to the carbon substituted with a methoxycarbonyl group appeared at higher field than that bonded to the carbon atom substituted with phenyl group. So we suggest the corresponding structure, (η^5-cyclopentadienyl)(η^4-1,1-diphenyl-2-methoxycarbonyl-3-methyl-4-*syn*-methoxycarbonylbutadiene)cobalt, because the vinylic proton resonance in this complex appeared at δ 0.36 ppm.



(VII)

Synthesis of butadiene complexes through reactions of this type will be a subject of the following paper [7].

Experimental

All reactions were carried out under nitrogen. Melting points were determined on a Mitamura micro melting point apparatus and were uncorrected. For column chromatography, Sumitomo Activated Alumina KCG-30 was used.

NMR spectra were obtained on a Varian HA-100B or a JEOL C-60HL spectrometer using tetramethylsilane as an internal reference in $CDCl_3$. Mass spectra were measured on a Niphondenshi JPS-1S mass spectrometer with direct inlet system at 75 eV. (η^5-Cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes were prepared according to the previously described method [4].

Preparation of (η^5-benzylcyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes

(1) (η^5-Benzylcyclopentadienyl)(triphenylphosphine)tetraphenylcobaltacyclopentadiene (I). To a suspension of $(PPh_3)_3CoCl$ (5 g, 5.7 mmol) in benzene (10 ml) was added lithium benzylcyclopentadienide (prepared from 10 mmol of PhLi and 10 mmol of benzylcyclopentadiene) in ether (20 ml). The mixture immediately turned dark-red. After 1 h, it was hydrolyzed and the resulting organic layer was dried with sodium sulfate. Diphenylacetylene (2 g, 11 mmol) was added to the filtered dark-red solution and the mixture was allowed to stand for 2 days at room temperature. After concentration, the residue was chromatographed on alumina. From the benzene eluate, dark-brown crystals of I were obtained (2.6 g, 3.1 mmol).

(2) (η^5-Benzylcyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene (II) and (η^5-benzylcyclopentadienyl)-(triphenylphosphine)-2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene (III). To a solution of (η^5-benzylcyclopentadienyl)bis(triphenylphosphine)-cobalt, which was prepared by the procedure described above (ca. 5 mmol solution), was added methyl phenylpropiolate (1.6 g, 10 mmol) and the mixture was allowed to stand overnight. After concentration, the residue was chromatographed on alumina. The red-brown benzene eluate was concentrated and hexane was added to give a mixture of red-brown crystals and dark-brown crystals. The large crystals were separated mechanically and the small crystals were dissolved in benzene and recrystallized again. Repetition of this procedure gave red-brown crystals of VI (0.27 g, 0.44 mmol) and dark-brown crystals of II (0.37 g, 0.46 mmol). Work-up of an orange-brown benzene/AcOEt (3/1) eluate gave dark-brown crystals of III (0.61 g, 0.76 mmol).

Physical properties of these cobaltacyclopentadiene complexes are summarized in Table 1.

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF $(\eta^5\text{-PhCH}_2\text{C}_5\text{H}_4)(\text{Ph}_3\text{P})(\overline{\text{CoCR}^1\text{=CR}^2\text{CR}^3\text{=C}}\text{R}^4)$

Compound					Analysis found (calcd.) (%)		M.p. ($^\circ$C)	^{1}H NMR (δ, ppm)[a]	
No.	R^1	R^2	R^3	R^4	C	H		CH_2[b]	OCH_3
I	Ph	Ph	Ph	Ph	83.58 (83.64)	5.83[c] (5.57)	141—142	3.55	
II	Ph	$COOCH_3$	Ph	$COOCH_3$	75.86 (75.37)	5.51 (5.31)	192—194	3.69[d]	2.90 3.12
III	Ph	$COOCH_3$	$COOCH_3$	Ph	75.57 (75.37)	5.38 (5.31)	169—171	3.03	3.33

[a] η^5-Cyclopentadienyl and phenyl protons appeared as multiplets. [b] $J(PH) \simeq 1$ Hz. [c] Recrystallized from CH_2Cl_2/cyclohexane. [d] AB type quartet ($J(AB)$ 15 Hz, $\delta_A - \delta_B$ 0.34 ppm).

TABLE 2. ANALYTICAL AND PHYSICAL DATA OF $(\eta^5\text{-RC}_5\text{H}_4)(\eta^4\text{-}\overline{\text{CR}^1\text{=CR}^2\text{CR}^3\text{=CR}^4})\text{Co}$

Compound					Analysis found (calcd.) (%)		Yield (%)	M.p. (°C)	^{1}H NMR[a] (δ, ppm)			
R	R^1	R^2	R^3	R^4	C	H			CCH$_3$	OCH$_3$	C$_5$H$_5$	Others
H	Ph	Ph	Ph	COOCH$_3$	75.42 (75.32)	5.16 (5.01)	80	159—160		3.80	4.74	
H	Ph	Ph	COOCH$_3$	COOCH$_3$	67.55 (67.57)	4.75 (4.76)	26	138		3.80	4.84	
H	Ph	COOCH$_3$	Ph	COOCH$_3$	67.84 (67.57)	4.70 (4.76)	27	175—178		3.72	4.80	
H	COOCH$_3$	CH$_3$	COOCH$_3$	Ph	62.87 (62.84)	4.98 (5.01)	18	121	2.16	3.76	4.74	
H	Ph	Ph	CH$_3$	COOCH$_3$	72.54 (72.00)	5.41 (5.29)	36	oil	2.16	3.76	4.67	
CH$_3$	Ph	Ph	COOCH$_3$	COOCH$_3$	68.21 (68.13)	5.13 (5.06)	33	132—133	1.73	3.80		4.58—4.76 (C$_5$H$_4$, m)
CH$_2$Ph	Ph	Ph	Ph	Ph	84.19 (84.20)	5.59 (5.48)	17	199—200				3.14(CH$_2$) 4.58(C$_5$H$_4$)

[a] All resonances are single unless otherwise stated. Phenyl protons are omitted.

TABLE 3. ANALYTICAL AND PHYSICAL DATA OF $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\overline{\text{C}_6\text{H}_4)(\eta^4\text{-C}}\text{Ph=CR}^1\text{CR}^2\text{=CHR}^3)\text{Co}$

Compound				Analysis found (calcd.) (%)		Yield (%)	M.p. (°C)	^{1}H NMR[a] (δ, ppm)		
No.	R^1	R^2	R^3	C	H			=CH	CH$_2$[b]	OCH$_3$
IV	Ph	Ph	Ph	84.28 (84.20)	5.52 (5.48)	38	283—288	1.81	3.98 (17 Hz, $\delta_A - \delta_B$ 0.34 ppm)	
V	COOCH$_3$	Ph	COOCH$_3$	72.31 (71.91)	5.16 (5.09)	49	254—255	0.52	3.95 (16 Hz, $\delta_A - \delta_B$ 0.38 ppm)	3.22 3.36
VI	COOCH$_3$	COOCH$_3$	Ph	72.13 (71.91)	5.00[c] (5.09)	82	248—251	1.21	3.85 (16 Hz, $\delta_A - \delta_B$ 0.35 ppm)	3.49 3.69

[a] Phenyl and cyclopentadienyl protons are omitted. [b] AB type pattern. [c] Recrystallized from aceton.

Preparation of (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt complexes

(1) (η^5-Cyclopentadienyl)(triphenylphosphine)-1,2,4-triphenyl-3-methoxycarbonylcobaltacyclopentadiene (0.10 g, 0.14 mmol) was heated in an evacuated tube at 220°C for 10 min. The melted mass was dissolved in benzene and chromatographed on alumina. A yellow benzene eluate was evaporated to dryness and crystallized from hexane to give yellow crystals of (η^5-cyclopentadienyl)(η^4-methoxycarbonyltriphenylcyclobutadiene)cobalt (0.51 g, 0.11 mmol).

Using this procedure, (η^5-cyclopentadienyl)(η^4-*cis*-diphenyl-methoxycarbonylmethylcyclobutadiene)cobalt and (η^5-methylcyclopentadienyl)(η^4-*cis*-diphenyldimethoxycarbonylcyclobutadiene)cobalt were obtained.

(2) (η^5-Cyclopentadienyl)(triphenylphosphine)-2,4-dimethoxycarbonyl-3-methyl-5-phenylcobaltacyclopentadiene (0.065 g, 0.10 mmol) in benzene (15 ml) was heated at 150°C for 7 h in a sealed tube. After cooling the solution was chromatographed on alumina. A yellow band was eluted with benzene/CH_2Cl_2 (1/1). The solvent was evaporated to dryness. Crystallization of the residue from hexane gave orange crystals of (η^5-cyclopentadienyl)(η^4-*trans*-dimethoxycarbonylmethylphenylcyclobutadiene)cobalt (0.007 g). A red-violet band was also eluted by the same mixed solvent and the eluate was evaporated to dryness. Crystallization of the residue from hexane gave dark-red crystals of VII (0.001 g, m.p. 136—138°C). NMR (δ, ppm): 0.36 (=CH), 2.60 ($C—CH_3$), 3.54, 3.66 ($O—CH_3$), 4.73 (C_5H_5), 6.5—7.9 (C_6H_5).

Using the procedure above, (η^5-cyclopentadienyl)(η^4-*cis*-diphenyl-dimethoxycarbonylcyclobutadiene)cobalt and (η^5-cyclopentadienyl)(η^4-*trans*-diphenyldimethoxycarbonylcyclobutadiene)cobalt were obtained,

Physical properties of the cyclobutadiene complexes thus obtained are summarized in Table 2.

Thermolysis of (η^5-benzylcyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes

(1) Compound I (0.21 g, 0.25 mmol) was heated in an evacuated tube at 160°C for 20 min. The melted mass was dissolved in benzene and chromatographed on alumina. A benzene/hexane (1/1) eluate was concentrated and hexane was added to give brick-red crystals of IV (0.054 g). From the mother liquid, yellow crystals of (η^5-benzylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt were obtained (0.025 g).

(2) Compound II (0.31 g, 0.39 mmol) was heated at 190°C for 5 min in an evacuated tube. The melted mass was dissolved in benzene and chromatographed on alumina. An orange-red eluate by benzene/CH_2Cl_2 (1/1) was concentrated and hexane was added to give red crystals of V (benzene solvated, 0.195 g). For the X-ray crystal structure analysis, they were recrystallized from acetone. Using this procedure, VI was obtained from III.

Physical properties of these butadiene complexes are summarized in Table 3.

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