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# COBALT METALLOCYCLES

## I. ONE-STEP AND STEPWISE SYNTHESIS OF COBALTACYCLOPENTADIENE COMPLEXES FROM ACETYLENES

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### Summary

($\pi$-Cyclopentadienyl) (triphenylphosphine) cobaltacyclopentadiene complexes having a variety of substituents have been prepared from substituted acetylenes and ($\pi$-cyclopentadienyl)bis(triphenylphosphine)cobalt. In some cases monoacetylene complexes have been isolated and by addition of other acetylenes to the monoacetylene complexes, cobalt metallocycles consisting of two different acetylene units have been prepared. The structures of all cobaltacyclopentadiene isomers have been determined by NMR spectra and/or by degradation to organic compounds.

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After the discovery of ferracyclopentadiene complexes, which are prepared by the reaction of iron carbonyl with acetylenes [1], many metallocyclopentadiene complexes have been prepared from acetylenes [2]. However, only few examples are known of the synthesis of complexes bearing different substituents in their metallocycles [1,2b,2d,2k]. Some metallocyclopentadiene complexes have been used as starting materials for the synthesis of 5- or 6-membered organic ring compounds [2b,3] and control of substitution in these organic ring compounds has been achieved by using cobaltacyclopentadiene complexes having various substituents at the desired positions in the metallocycle [3].

In the present paper, we report details of the synthesis of such substituted cobaltacyclopentadiene complexes. They are prepared in one step by the reaction of ($\pi$-cyclopentadienyl)bis(triphenylphosphine)cobalt with two molar equivalents of a substituted acetylene or, by a stepwise procedure, with isolation of intermediate ($\pi$-acetylene)cobalt complexes. By the stepwise method two different acetylenes can be incorporated into the metallocycle.

TABLE 1

COBALTACYCLOPENTADIENE COMPLEXES

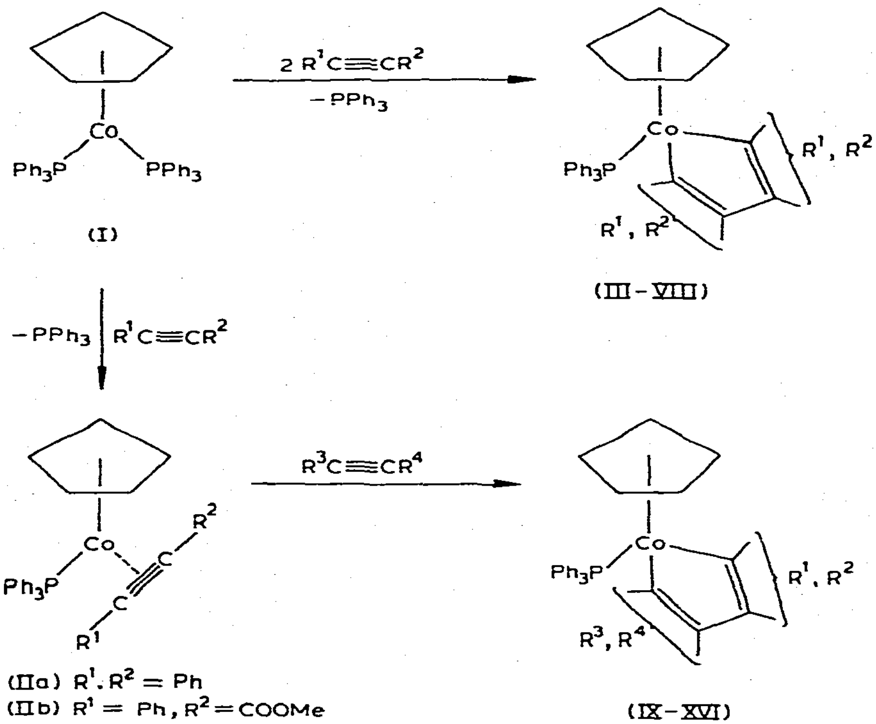
| Compound | $\overline{Co-CR^1=CR^2-CR^3=CR^4}$ R[1] | R[2] | R[3] | R[4] | Yield (%) | M.p. (°C) | Analysis found (calcd.) (%) C | H | NMR (δ ppm) in $CDCl_3$ $C_5H_5$ | O—Me | C—Me |
|---|---|---|---|---|---|---|---|---|---|---|---|
| III | Ph | Ph | Ph | Ph | 88 | 193–194 | 82,57(82,47) | 5,57(5,43) | 4,82 | | |
| IV | COOMe | COOMe | COOMe | COOMe | 14 | 216–217 | 62,56(62,70) | 4,86(4,81) [a] | 5,06 | 3,56 3,45 | |
| | | | | | | | 64,59(64,32) | 5,02(4,97) [b] | | | |
| V | $CH_2OMe$ | $CH_2OMe$ | $CH_2OMe$ | $CH_2OMe$ | 36 | 105–106 | 68,81(68,40) | 6,40(6,56) | 4,97 | 3,21 3,16 [d] | |
| VI-1 | Ph | COOMe | Ph | COOMe | 29 | 215–217 | 72,92(73,09) | 5,27(5,14) | 4,92 | 3,06 3,03 | |
| VI-2 | Ph | COOMe | COOMe | Ph | 26 | 218–219 | 73,26(73,09) | 5,28(5,14) | 4,75 | 3,32 | |
| VII-1 | COOMe | Me | Me | COOMe | 9 | 192–194 | 68,33(68,04) | 5,77(5,54) | 4,98 | 3,46 | 1,50(2 Hz) |
| VII-2 | COOMe | Me | COOMe | Me | 50 | 158–160 | 68,25(68,04) | 5,55(5,54) | 4,94 | 3,57 3,40 | 1,65(2 Hz) 2,47 |
| VIII | Ph | Me | Me | Ph | 54 | 174–176 | 80,96(81,02) | 6,11(6,08) [c] | 4,64 | | 1,61(1 Hz) |
| IX | Ph | Ph | COOMe | COOMe | 48 | 119–121 | 73,41(73,08) | 5,27(5,14) | 4,95 | 3,46 3,20 | |
| X | Ph | Ph | $CH_2OMe$ | $CH_2OMe$ | 40 | 174–176 | 76,44(76,10) | 6,04(5,94) | 4,85 | 3,18 3,10 [e] | |
| XI | Ph | Ph | H | Ph | 27 | 180–182 | 81,14(81,06) | 5,63(5,44) | 4,82 | | |
| XII | Ph | Ph | H | COOMe | 48 | 149–151 | 76,96(76,86) | 5,59(5,42) [c] | 4,89 | 3,43 | |
| XIII | Ph | Ph | Me | Ph | 67 | 169–171 | 81,40(81,17) | 5,65(5,63) | 4,72 | | 1,59(1 Hz) |
| XIV | Ph | Ph | Me | COOMe | 68 | 180–182 | 75,88(76,13) | 5,61(5,48) | 4,89 | 3,17 | 1,82(2 Hz) |
| XV-1 | Ph | Ph | Ph | COOMe | 5 | 217–218 | 78,18(77,89( | 5,39(5,29) | 5,07 | 2,96 | |
| XV-2 | Ph | Ph | COOMe | Ph | 43 | 210 | 77,78(77,89) | 5,22(5,29) | 4,90 | 3,22 | |
| XVI-1 | COOMe | Me | Ph | COOMe | 9 | 202–203 | 70,59(70,81) | 5,60(5,32) | 5,03 | 3,34 3,16 | 1,63(2 Hz) |
| XVI-2 | COOMe | Me | COOMe | Ph | 39 | 179–182 | 70,67(70,81) | 5,24(5,32) | 4,89 | 3,30 3,16 | 1,86(2 Hz) |

[a] Dried at 170° under reduced pressure. [b] Solvated with $C_6H_6$. [c] Solvated with $\frac{1}{2}CH_2Cl_2$. [d] PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 ($J_{AB}$ 10 Hz, $\delta_A - \delta_B$ 0.21 ppm) and as one broad singlet at 3.73 ppm. [e] PMR of $-CH_2-O$'s appear as two AB patterns centered at 3.92 ($J_{AB}$ 11 Hz, $\delta_A - \delta_B$ 0.48 ppm) and at 3.76 ppm ($J_{AB}$ 10 Hz, $\delta_A - \delta_B$ 0.08 ppm).

## Results and discussion

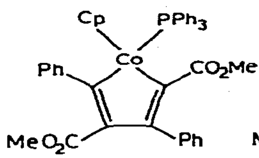
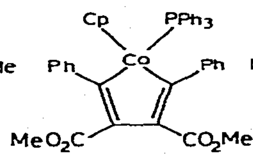
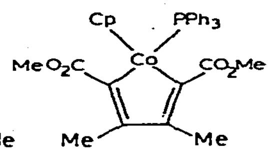
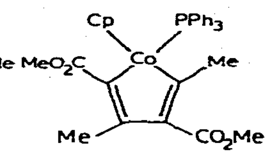
The reaction is illustrated in Scheme 1 and all the cobaltacyclopentadiene complexes thus obtained are summarized in Table 1. They are very stable at room temperature and their solutions can be handled in air. However, they react easily with diverse reagents at 70—110°C [3]. In particular, the substituted thiophenes and benzenes derived from them are helpful for the determination of the position of each substituent in the parent cobalt metallocycles.

SCHEME 1




The reaction of ($\pi$-cyclopentadienyl)bis(triphenylphosphine)cobalt (I) with an equimolar amount of diphenylacetylene or methyl phenylpropiolate gave the ($\pi$-acetylene)cobalt complex (IIa, IIb) in good yield, whereas, a similar reaction with excess of acetylene afforded cobaltacyclopentadiene complexes (III—VIII).

In the one-step synthesis using methyl phenylpropiolate, the resulting complex contained only two of the three possible isomers and these were separated by column chromatography. Complex VI-1, which was eluted faster than the other, shows two methyl PMR absorptions and was assigned the structure ($\pi$-cyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene. The other isomer, VI-2, which revealed only one kind of methyl resonance in the PMR spectrum and gave 2,5-diphenyl-3,4-dimethoxycarbonylthiophene [4] on treatment with sulfur, was assigned as 2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene.

(VI-1) (VI-2) (VII-1) (VII-2)

Cp = $C_5H_5$

The reaction of I with an excess of methyl methylpropiolate also gave two isomers. Complex VII-1, which was eluted faster than the other from an alumina column, has only two kinds of methyl resonances at $\delta$ 1.50 (d, $J$ 2 Hz, C—$CH_3$) and 3.46 (s, O—$CH_3$) ppm and gave 2,5-dimethoxycarbonyl-3,4-dimethylthiophene [5] on treatment with sulfur. It was, therefore, assigned the structure 2,5-dimethoxycarbonyl-3,4-dimethylcobaltacyclopentadiene. Another complex, VII-2, which shows four methyl resonances at $\delta$ 1.65 (d, $J$ 2 Hz, C—$CH_3$), 2.47 (s, C—$CH_3$), 3.40 (s, O—$CH_3$), and 3.57 (s, O—$CH_3$) ppm, was assigned as 2,4-dimethoxycarbonyl-3,5-dimethylcobaltacyclopentadiene derivative.

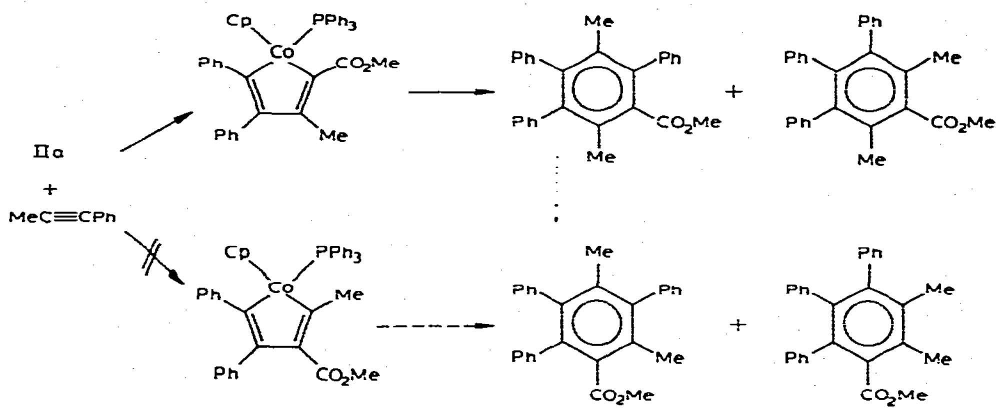
It is noteworthy that the methyl proton resonances at $\delta$ 1.50 in VII-1 and at 1.65 in VII-2 appear as doublets due to coupling with the $^{31}P$ nucleus, whereas the other C—$CH_3$ resonance in VII-2 appears as a singlet. The finding that the long-range $^1H$-$^{31}P$ coupling occurs only in the methyl group attached to 3- or 4-position of the cobaltacyclopentadiene ring supplies a method for the structural elucidation of other related complexes. The structure of VIII, which was the sole product in the reaction of I with methylphenylacetylene, was determined on this basis as that of 2,5-diphenyl-3,4-dimethylcobaltacyclopentadiene since the methyl resonance appears as a single doublet at $\delta$ 0.61 ($J$ 1 Hz) ppm. This structure was further supported by the thiophene and benzene derivatives derived by the reaction of VIII with sulfur or dimethyl acetylenedicarboxylate: the melting points of the thiophene (159°C) and the benzene (126—127°C) derivatives obtained differed from those of known 2,5-dimethyl-3,4-diphenylthiophene (m.p. 113—114°C) [6] and 1,2-dimethoxycarbonyl-3,6-dimethyl-4,5-diphenylbenzene (m.p. 212°C) [7].

Cobaltacyclopentadiene complexes also were prepared from IIa and IIb. The reaction of IIa with dimethyl acetylenedicarboxylate and 1,4-dimethoxybutyne-2 gave IX and X, respectively. The reaction of IIa with unsymmetrical acetylenes, such as phenylacetylene, methyl propiolate, methylphenylacetylene, and methyl methylpropiolate, gave only one isomer (complexes XI—XIV, respectively) of the possible two.

From complexes XI and XII known thiophenes [4a,8,9] were derived by treatment with sulfur, thereby determining the positions of substituents in these metallocycles as indicated in Table 1. The structures of XIII and XIV could be deduced from their PMR spectra: doublet peaks of C—$CH_3$ groups with coupling constant 1 Hz in XIII and 2 Hz in XIV indicated that the C—$CH_3$ groups were attached to the $\beta$-carbon of the cobaltacycle. The structure of XIV was further confirmed by its reaction with methylphenylacetylene, which gave a ca. 1 : 1

mixture of benzene derivatives (Scheme 2). In the PMR spectrum, one of the benzene isomers showed a single peak due to the C—$CH_3$ group at $\delta$ 2.09 ppm and the other isomer showed resonances at $\delta$ 2.05 and 1.80 ppm. The alternate structure for XIV would not give benzenes having such a resonance pattern (Scheme 2).

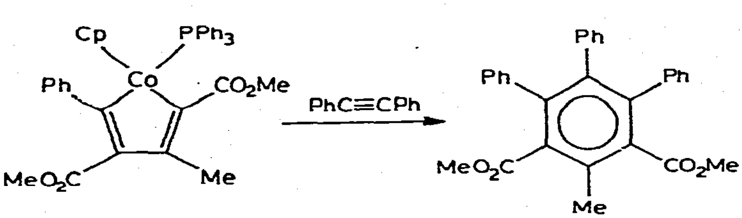
SCHEME 2




The reaction of IIa with methyl phenylpropiolate gave both isomers, XV-1 (5% yield) and XV-2 (43%). Based on the melting point of the thiophene derived from XV-2, which was consistent with that of authentic 2,3,5-triphenyl-4-methoxycarbonylthiophene [4a], the structures of both isomers were deduced as shown in Table 1.

The reaction of IIb with methyl methylpropiolate yielded only two isomers, XVI-1 and XVI-2. Their PMR spectra show doublet peaks attributable to C—$CH_3$ groups with a coupling constant of 2 Hz, suggesting that the methyl group is bonded to the $\beta$-carbon of the metallocycle in both isomers. As the melting point of the thiophene obtained from XVI-1 coincided with that of literature value [4a], XVI-1 was determined to be the 2,5-dimethoxycarbonyl-3-methyl-4-phenylcobaltacyclopentadiene derivative. The structure of XVI-2 was confirmed by a PMR spectrum of the benzene derivative prepared by its reaction with diphenylacetylene. Only one of the four possible isomers should give a benzene having a single O—methyl resonance and that was the case (Scheme 3).

SCHEME 3



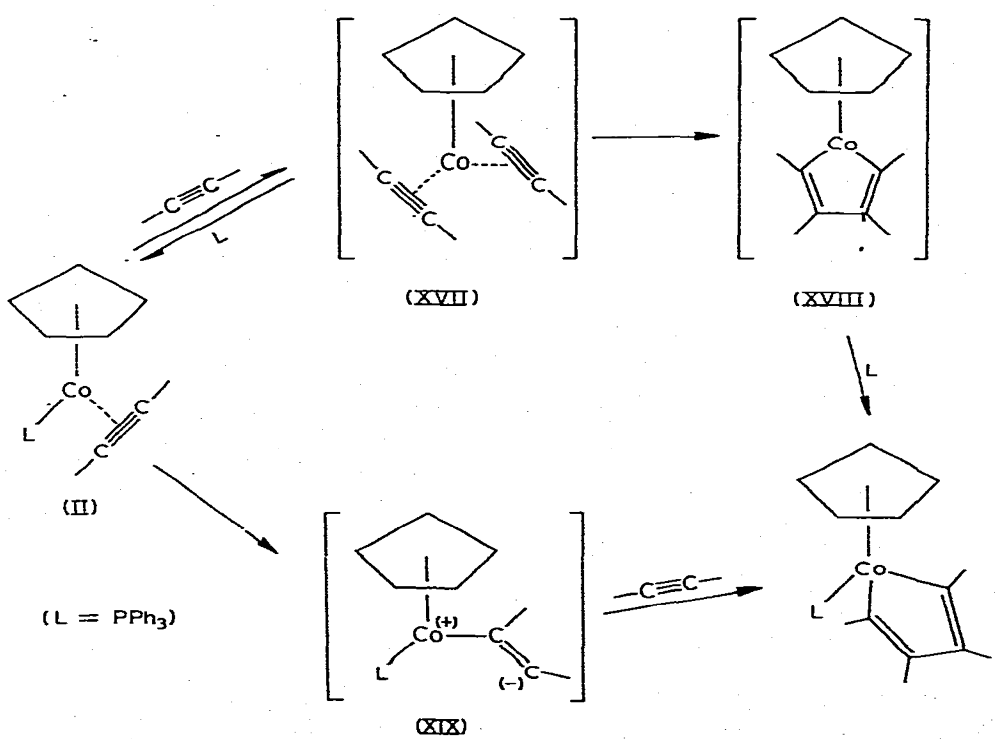

(XVI-2)

Obviously, the first step of the cobaltacyclopentadiene formation from I is replacement of one of the phosphines by an acetylene molecule to form a $\pi$-

acetylene complex II. For further reaction of II with an acetylene, two alternatives may be proposed (Scheme 4). In the first of these (path-1), an attacking acetylene replaces the other phosphine to give a bis(acetylene) complex (XVII), which undergoes oxidative coupling to form a coordinatively unsaturated $Co^{III}$ metallocycle XVIII. Similar types of intermediate have been proposed in the reaction of "titanocene" with olefins [10] or diphenylacetylene [11]. The second path includes a thermally excited, ionic *monohapto*-acetylene intermediate XIX [1f,1j] to supply a vacant coordination site for an attacking acetylene molecule.

It is difficult to distinguish between these alternatives, but path-1 seems more probable by the following reasoning, although the ionic *monohapto*-acetylene intermediate might be important in other systems in which a much polar molecule is incorporated into a metallocycle [12]. (*1*) Polar solvents such as dichloromethane or pyridine did not enhance the rate of the reaction, IIa + $Ph_2C_2 \rightarrow$ III, which could be observed easily by disappearance of the characteristic green color of IIa. (*2*) The reactions of IIa with methyl phenylpropiolate, and of IIb with diphenylacetylene, gave cobaltacyclopentadienes XV-1 and XV-2 in virtually identical ratio. The result, together with that of *1*, suggests that a polar intermediate XIX is improbable. (*3*) Addition of free triphenylphosphine to a reaction system of IIa with diphenylacetylene markedly decreased the rate. The observation can be interpreted by the reasonable assumption that XVII → XVIII

SCHEME 4



is the rate determining step of path-1 and that preliminary equilibrium is attained between II and XVII. To accomodate this observation, the ligand (triphenylphosphine) should not participate in the oxidative coupling reaction of the bisacetylene complex.

When asymmetrically substituted acetylenes are used, the positions of the substituents in the final cobalt metallocycle will be governed by arrangements of the two acetylene molecules in the bisacetylene intermediate XVII, which might largely be affected by a dipole—dipole interaction between them. Which carbon of each acetylene unit is bonded to cobalt in the oxidative coupling step to give the more thermodynamically stable isomer, would be another important factor in determining regioselectivity of the final product.

## Experimental

All reactions were performed under nitrogen. Melting points are uncorrected and determined on a Mitamura micromelting point apparatus. For column chromatography, Sumitomo Activated Alumina KCG-30 was used. IR spectra were obtained on a Shimazu IR-27G spectrophotometer. PMR spectra were recorded on a Varian HA-100 or a JEOL-60 spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra were obtained on a Niphondenshi JPS-IS spectrometer at 75 eV.

### *(π-Cyclopentadienyl)bis(triphenylphosphine)cobalt (I)*

The following improved method was employed instead of the known published method [13].

To freshly prepared chlorotris(triphenylphosphine)cobalt [14] (12 g, 13.6 mmol) suspended in benzene (160 ml) was added a tetrahydrofuran solution of sodium cyclopentadienide (1 mmol solution, 20 ml) at room temperature, and the resulting dark-red solution was stirred for 30 min. Excess of sodium cyclopentadienide then was hydrolyzed with water (10 ml) at 0°C and the organic layer was dried over sodium sulfate. Concentration of the filtered solution under pressure (to ca. 30 ml), followed by addition of hexane (30 ml), gave dark-red crystals of the desired complex in 24 h (6.9 g, 70% yield).

### *(π-Acetylene)cobalt complexes (III)*

*(π-Cyclopentadienyl)(π-diphenylacetylene)(triphenylphosphine)cobalt (IIa).* The known method [15] was improved as follows. Diphenylacetylene (0.9 g, 5 mmol) was added to a solution of I (3.6 g, 5 mmol) in benzene (25 ml) and the reaction mixture was allowed to stand at room temperature. After 1 h, hexane (50 ml) was added to precipitate shiny black crystals of the title compound which were separated by decantation and washed with hexane (2.4 g, 85%). The crystals should be stored in a refrigerator.

*(π-Cyclopentadienyl)(π-methyl phenylpropiolate)(triphenylphosphine)cobalt (IIb).* To a solution of I (1.3 g, 1.8 mmol) in benzene (50 ml) was added methyl phenylpropiolate (0.3 g, 1.9 mmol) at 0°C and the solution was allowed to stand overnight at room temperature. After concentration, the residue was

TABLE 2

THIOPHENES

| Parent cobalt complex | $\overline{S-CR^1=CR^2-CR^3=CR^4}$ R¹ | R² | R³ | R⁴ | Yield (%) | M.p. (°C) (lit. value) | PMR in $CDCl_3$ (δ, ppm) O–Me | C–Me | Analysis found (calcd.) (%) C | H | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VI-2 | Ph | COOMe | COOMe | Ph | 58 | 166 –167 [a]<br>(166 –167.5) [b]<br>(167 –168) [c] | 3.80 | | 68.43<br>(68.17) | 4.48<br>(4.58) | 9.18<br>(9.10) |
| VII-1 | COOMe | Me | Me | COOMe | 31 | 168 –169 [d]<br>(170 –171) [e]<br>(171.5–172.5) [f] | 3.86<br>(3.85) | 2.46<br>(2.44) [e] | 52.61<br>(52.62) | 5.27<br>(5.30) | 13.85<br>(14.05) |
| VIII | Ph | Me | Me | Ph | 70 | 159 [g] | | 2.22 | 81.99<br>(81.77) | 5.95<br>(6.10) | 12.17<br>(12.13) |
| XI | Ph | Ph | H | Ph | 24 | 139 –140 [h]<br>(142 –143) [b] | | | 84.62<br>(84.58) | 4.96<br>(5.16) | |
| XII | Ph | Ph | H | COOMe | 46 | 96.5 | 3.89 | | 73.50<br>(73.44) | 4.80<br>(4.79) | |
| | Ph | Ph | H | COOEt [i] | 22 | 78<br>(77.5) [j] | | | 73.98<br>(74.00) | 5.30<br>(5.23) | |
| XV-2 | Ph | Ph | COOMe | Ph | 76 | 138 –139<br>(138 –139) [b] | 3.48 | | 78.06<br>(77.81) | 4.71<br>(4.90) | 8.66<br>(8.66) |
| XVI-1 | COOMe | Me | Ph | COOMe | 31 | 135 [k]<br>(134.5–135) [b] | 3.70<br>3.90 | 2.28 | 61.78<br>(62.05) | 4.92<br>(4.86) | |
| XVI-2 | COOMe | Me | COOMe | Ph | 41 | 97 –98 | 3.67<br>3.86 | 2.64 | 62.38<br>(62.05) | 4.87<br>(4.86) | 10.95<br>(11.04) |

[a] Compare with 2,5-dimethoxycarbonyl-3,4-diphenylthiophene, m.p. 187–188°C [16]. [b] [4a]. [c] [4b]. [d] Compare with 2,5-dimethyl-3,4-dimethoxycarbonylthiophene, m.p. 63–64°C [17]. [e] [5a]. [f] [5b]. [g] Compare with 2,5-dimethyl-3,4-diphenylthiophene, m.p. 113–114°C [6]. [h] Compare with 2,3,4-triphenylthiophene, m.p. 215–216°C [18]. [i] Prepared by ester exchange reaction of the methyl ester analogue derived from XII. PMR of the ring-H appears at δ 7.82 and that of ethyl group at 4.37 (q., $J$ 7 Hz, O–$CH_2$) and 1.38 (t., $J$ 7 Hz, C–$CH_3$). [j] [9]. [k] Compare with 2-methyl-3,4-dimethoxycarbonyl-5-phenylthiophene, m.p. 78–79.5°C [4a].

chromatographed on $Al_2O_3$ (2 × 15 cm). A brown-red band was eluted with benzene. Concentration and addition of hexane gave chocolate-brown crystals of the title complex (0.73 g, 74%), m.p. 131—133°C (dec.). Found: C, 72.64; H, 5.20; mol. wt. 521 (vapor pressure osmometry in benzene). $C_{33}H_{28}O_2PCo$ calcd.: C, 72.53; H, 5.16%; mol. wt. 546.5. PMR ($C_6D_6$): δ 3.57 (s, $CH_3$); 4.74 (s, $C_5H_5$); 7—8 (multiplet, Ph) ppm. IR (nujol mull): 1820 $\nu$(C≡C) $cm^{-1}$.

*Cobaltacyclopentadiene complexes (III—XVI)*

*(π-Cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetramethoxycarbonylcobaltacyclopentadiene (IV).* To a solution of I (1.5 g, 2.1 mmol) in benzene (20 ml) was added dimethyl acetylenedicarboxylate (1.1 g, 8 mmol in 10 ml of benzene) dropwise under ice-cooling. The mixture was allowed to stand overnight at room temperature and then was chromatographed on $Al_2O_3$. An orange-red band was eluted with 1 : 1 benzene/ethyl acetate. Removal of the solvent in vacuo and treatment of the residue with benzene/hexane gave orange-red crystals of IV (solvated with $\frac{1}{2}$ mol of benzene, 0.25 g, 14%). The solvated benzene could be removed by heating the crystals in vacuo at 170°C for 30 min.

*(π-Cyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene (VI-1) and (π-cyclopentadienyl)(triphenylphosphine)-2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene (VI-2).* To a solution of I (6.0 g, 8.3 mmol) in benzene (90 ml) was added methyl phenylpropiolate (3.0 g, 18.8 mmol) and the mixture was allowed to stand overnight. After concentration, the reaction mixture was chromatographed on $Al_2O_3$. Two bands separated on elution with 25 : 1 benzene/tetrahydrofuran. The first red-brown band was collected, concentrated and hexane was added to give red-brown crystals of VI-1 (1.7 g, 29%). From the second orange band, which was eluted with 10 : 1 benzene/tetrahydrofuran, orange-brown crystals of VI-2 were obtained (1.5 g, 26%).

By similar procedures, VII-1, VII-2, and VIII were prepared and isolated.

*(π-Cyclopentadienyl)(triphenylphosphine)-2,3-diphenyl-4-methyl-5-methoxycarbonylcobaltacyclopentadiene (XIV).* To a solution of IIa (0.56 g, 1 mmol) in benzene (20 ml) was added methyl methylpropiolate (0.15 ml). After 1 h, the mixture was concentrated and chromatographed on $Al_2O_3$. A brown band eluted with 10 : 1 benzene/dichloromethane was collected and concentrated. Addition of hexane gave brown crystals of XIV (0.45 g, 68%).

By similar procedures, were obtained IX, X, XI, XII, XIII, XV-1, and XV-2.

*(π-Cyclopentadienyl)(triphenylphosphine)-2,5-dimethoxycarbonyl-3-methyl-4-phenylcobaltacyclopentadiene (XVI-1) and (π-cyclopentadienyl)(triphenylphosphine)-2,4-dimethoxycarbonyl-3-methyl-5-phenylcobaltacyclopentadiene (XVI-2).* Methyl methylpropiolate (0.25 ml) was added to a solution of IIb (1.1 g, 2 mmol) in benzene (30 ml). After it had stood overnight, the reaction mixture was concentrated and chromatographed on $Al_2O_3$ to give mainly three zones, red-violet, yellow, and orange in color. From the first zone, which was eluted with 1 : 1 benzene/dichloromethane, dark-red crystal, which did not contain the triphenylphosphine ligand and of as yet unknown structure, were obtained (0.014 g, m.p. 136—138°C). Collection and concentration of the second band, which was eluted with dichloromethane, followed by addition of

hexane, gave orange-red crystals of XVI-1 (0.12 g, 9%). From the third zone, which was eluted with 4 : 1 benzene/ethyl acetate, brown crystals of XVI-2 were obtained by similar work-up (0.50 g, 39%).

### *Reaction with sulfur*

*Reaction of VI-2 with sulfur.* A mixture of VI-2 (0.20 g, 0.365 mmol) and elemental sulfur (80 mg) in benzene (30 ml) was heated at 150°C for 6 h in a sealed tube. After concentration, the reaction mixture was chromatographed on $Al_2O_3$ (2 × 15 cm). After the column was eluted with benzene (200 ml) and further with 1 : 1 benzene/dichloromethane (100 ml), the eluate with dichloromethane was collected and concentrated. The residue was crystallized from hexane to give colorless crystals of 2,5-diphenyl-3,4-dimethoxycarbonylthiophene.

Other reactions of cobaltacyclopentadiene complexes with sulfur were carried out similarly; Table 2 compares physical properties of thiophenes thus obtained with those listed in the literature.

### *Reaction with acetylenes*

*Reaction of VIII with dimethyl acetylenedicarboxylate.* A mixture of VIII (0.21 g, 0.32 mmol) and dimethyl acetylenedicarboxylate (0.15 ml) in benzene (10 ml) was heated at 70°C in a sealed tube. After 20 h, the reaction mixture was chromatographed on $Al_2O_3$ and the eluate with 1 : 1 benzene/dichloromethane was collected. Evaporation of the solvent and recrystallization of the residue from benzene/hexane gave colorless crystals of 1,2-dimethoxycarbonyl-3,6-diphenyl-4,5-dimethylbenzene (0.014 g, 13%) m.p. 126—127°C. Found: C, 77.24; H, 5.90. $C_{24}H_{12}O_4$ calcd.: C, 76.98; H, 5.92%.

*Reaction of XVI-2 with diphenylacetylene.* By a similar procedure to that described above, crystals of 1,2-dimethoxycarbonyl-2-methyl-4,5,6-triphenylbenzene were obtained (50 mg, 36%) from XVI-2 (205 mg, 0.29 mmol) and diphenylacetylene (0.33 g), m.p. 204—205°C. Found: C, 79.92; H, 5.60; mol. wt. 436 (mass spectrum). $C_{29}H_{24}O_4$ calcd.: C, 79.79; H, 5.54%; mol. wt. 436.5. PMR: $\delta$ 2.38 (C—$CH_3$); 3.45 (O—$CH_3$) ppm.

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