Cobalt Metallacycles. Part 9.† Some Reactions of Cobaltaindene, Cobaltafluorene, Cobaltaxanthen, and Cobaltacyclopentane Complexes
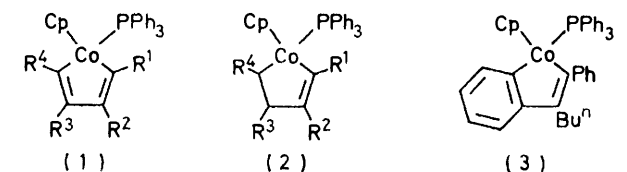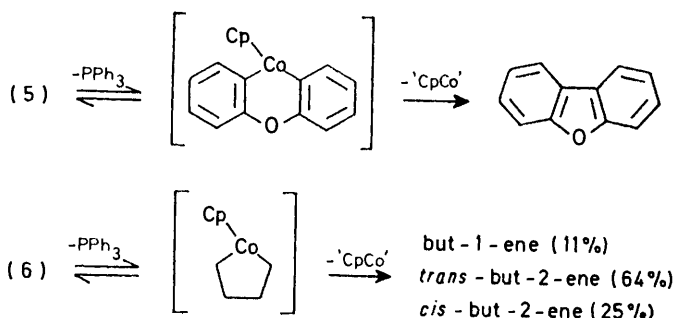
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The reactivity of the title compounds toward acetylenes, olefins, carbon monoxide, and isocyanides, as well as their behaviour on thermal decomposition, has been examined and compared with those of previously reported cobaltacyclopentadiene and cobaltacyclopentene. In most cases the unsaturated reactant is incorporated into the final organic product. The common first step in the reactant incorporation and the thermal decomposition is dissociation of ligating phosphine, the ease of which markedly depends on the nature of the metallacycle. Molecular orbital calculations on cobaltacyclopentadiene and cobaltacyclopentane have been carried out to interpret their reactivity. The calculated stabilization energy is found to be a good measure of the reactivity. A discussion of the metallaring expansion by insertion of ethylene is based on the concept of overlap populations between relevant carbon atoms.
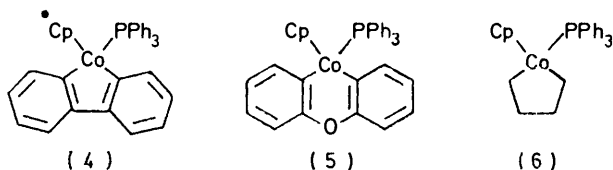
In earlier Parts, we have reported that cyclopentadienyl-(triphenylphosphine)cobaltacyclopentadiene complexes (1) react with a variety of reagents, e.g. acetylenes, olefins, carbon monoxide, and isocyanides to give the corresponding cyclic organic compounds and/or their complexes presumably via ring expansion of the cobalt metallacycle.[1] Cobaltacyclopentene complexes (2) show a similar reactivity with acetylenes, cyclohexadiene complexes being the product, while with olefins they give linear hexadiene derivatives, the formation of which has been accounted for by assuming intramolecular β-hydride transfer of a seven-membered cobalt metallacycle intermediate.[2] The unique reactivity of (1) and (2) led us to inquire whether other related cobalt metallacycles, which are different in Co–C bonding character and ring size, might behave similarly. In this paper, we describe the reactivity of η^5-cyclopentadienyl-(triphenylphosphino)-cobaltaindene (3), -cobaltafluorene

$$Cp = \eta^5-C_5H_5$$

(4), -cobaltaxanthen (5), and -cobaltacyclopentane (6) toward unsaturated reactants, together with their thermal degradation. Some results are interpreted by molecular orbital calculations.

RESULTS AND DISCUSSION

Complexes (3)—(5) were prepared by the reaction of η^5-cyclopentadienyl(di-iodo)(triphenylphosphine)cobalt

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with the corresponding dilithio or Grignard reagent in yields of 35—38%. Cobaltacyclopentane (6) was prepared according to the procedure described by Diversi *et al.*[3] Cobaltafluorene (4) has been prepared by Rausch *et al.* in a slightly different way.[4]

Thermal Stability and Dissociation of the Triphenylphosphine Derivatives.—Marked differences in thermal stability were found for these cobalt metallacycles. In

benzene solution, (3) and (4) began to decompose above 90 °C although attempts to isolate any organic products failed. In contrast, (5) and (6) in benzene decomposed at room temperature giving dibenzofuran and a mixture of butenes, respectively. In the latter case, cyclobutane and ethylene were not detected. The decomposition of (5), which clearly led to reductive coupling of the Co–C bonds, was examined in more detail. First, addition of triphenylphosphine to a solution of (5) was found to suppress the decomposition. For example, the recovery of 24% of (5) after 1 week in benzene solution increased to 82% when an equimolar amount of triphenylphosphine was added to the system initially. Secondly, quantitative exchange of the ligating triphenylphosphine with methyldiphenylphosphine under similar conditions (1 week at room temperature) was observed. It was therefore concluded that triphenylphosphine in (5) dissociates at room temperature and its dissociation is a prerequisite for Co–C bond splitting. This point will be discussed later in terms of molecular orbital theory. A similar inhibitory effect by added phosphine was observed in the decomposition of (6).
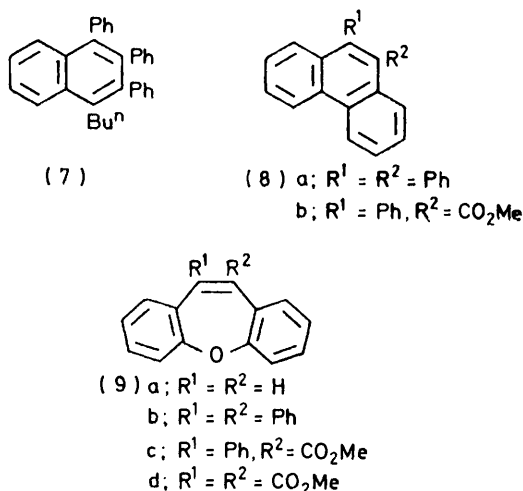
When an unsaturated reagent L (L = alkyne, alkene, CO, isocyanide) was added to the system instead of phosphine, it was incorporated in the final organic product which was possibly formed through the co-ordination of L to cobalt and successive metallacycle expansion as illustrated in the Scheme. The formation of intermediates (II) and (III) has been proposed based on kinetic data and X-ray crystallographic analyses for the reaction of (2) with olefins.[2]

The temperatures required for the reaction of L with metallacycles (1)—(6) were found to be different from
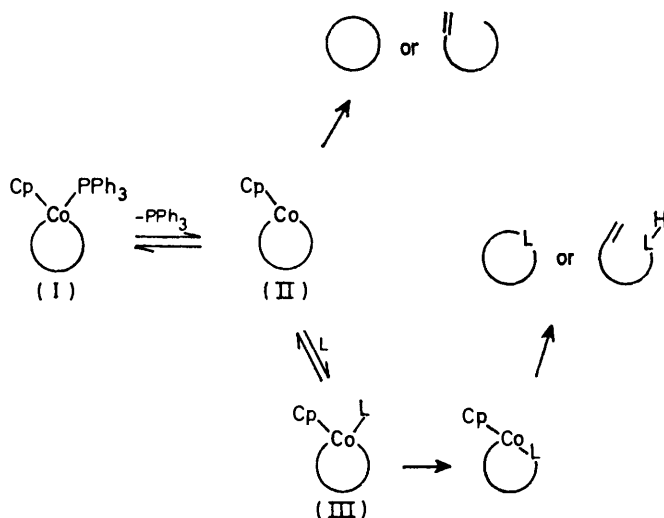
SCHEME

each other. Roughly they can be classified into two groups, (2), (5), and (6) which react at room temperature, and (1), (3), and (4) which react only at elevated temperatures (70—90 °C). The difference in these two groups can be attributed to the ease of phosphine dis-

(7)

(8) a; R^1 = R^2 = Ph
b; R^1 = Ph, R^2 = CO$_2$Me

(9) a; R^1 = R^2 = H
b; R^1 = R^2 = Ph
c; R^1 = Ph, R^2 = CO$_2$Me
d; R^1 = R^2 = CO$_2$Me

sociation, i.e. the formation of intermediate (II) in the Scheme, because the required temperatures for the reactions of L were parallel to those for the phosphine exchange reaction. The difference in the ease of phosphine

dissociation in these two groups will be discussed later on the basis of MO theory.

Reaction with Acetylenes.—Cobalt metallacycles (3)—(6), like (1)[1] and (2),[2] reacted smoothly with acetylenes.

(10)   (11)   (12)

(13)   (14)   (15)
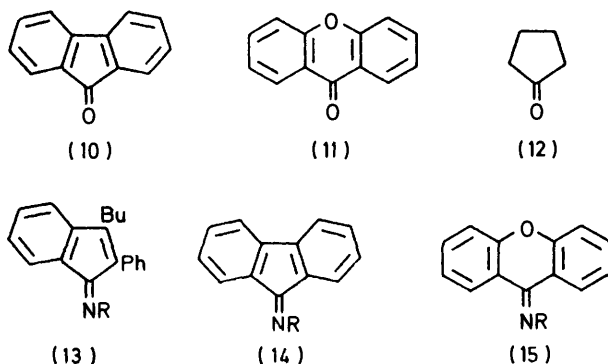
The reaction of (3) with diphenylacetylene led to a naphthalene derivative (7) (24%); the reaction of (4) with diphenylacetylene or methyl phenylpropiolate gave the phenanthrene derivatives (8a) (45%) and (8b) (61%). Likewise (5) and acetylenes [C$_2$H$_2$, C$_2$Ph$_2$, PhC$_2$CO$_2$Me, C$_2$(CO$_2$Me)$_2$] gave the dibenzoxepin derivatives (9a) (41%), (9b) (75%), (9c), (62%), and (9d) (26%). The reaction of the saturated metallacycle (6) and C$_2$H$_2$ gave hexa-1,5-diene (57%) which, we suppose, resulted from β-hydrogen transfer in the cobaltacyclo-heptene intermediate.

Reaction with Carbon Monoxide and Isocyanide.—

(16)
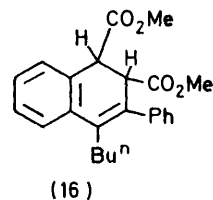
Incorporation of CO and isocyanide [5] into the final organic ring compounds appears to be a general phenomenon. The reaction of CO with (4)—(6) gave the respective cyclic ketones (10) (43%), (11) (25%), and (12) (33%) and that of R–NC (R = 2,6-Me$_2$C$_6$H$_3$) with (3)—(5) gave the iminocyclic compounds (13) (43%), (14) (44%), and (15) (30%).

Reaction with Olefins.—The combination of cobalt metallacycle and olefin afforded the expected products. Thus, dimethyl maleate reacted with (3) to give (16) in 58% yield and ethylene and (6) gave hex-1-ene (68%).

We conclude that the formation of new C–C bond(s) upon reacting cobalt metallacycles with acetylenes, olefins, CO, or isocyanide is a general reaction. However, we found that the reaction of olefins with (4)—(6) is more difficult than with (1), which with various olefins reacts quite smoothly.[6]

Molecular Orbital Calculations.—Extended Hückel calculations were carried out on cobaltacyclopentadiene (1) and cobaltacyclopentane (6) using PH$_3$ in the place of PPh$_3$ and assuming a quasi-octahedral conformation

around the cobalt atoms.* An 'opened envelope' conformation was assumed for the metallacycle portion in (6). The result was interpreted through a formalism which partitions the composite molecule into two fragments. Then stabilization energy which can be expected on uniting the two fragments was calculated according to Fukui, by equation (2) [8] where Δe_{ik} is the stabilization

$$\Delta E = \sum_{i}^{A} \sum_{k}^{B} \Delta e_{ik} \qquad (1)$$

energy calculated by interacting the ith MO in fragment A and the kth MO in fragment B.

Partitioning of (1) and of (6) into PH_3 and the remainder of the molecule revealed that phosphine is bound in (1) more strongly than in (6) [stabilization energy, 3.5 eV for (1), 3.1 eV for (6)], which is in agreement with the experimental observation that (1) loses phosphine above 70 °C and (6) at room temperature.
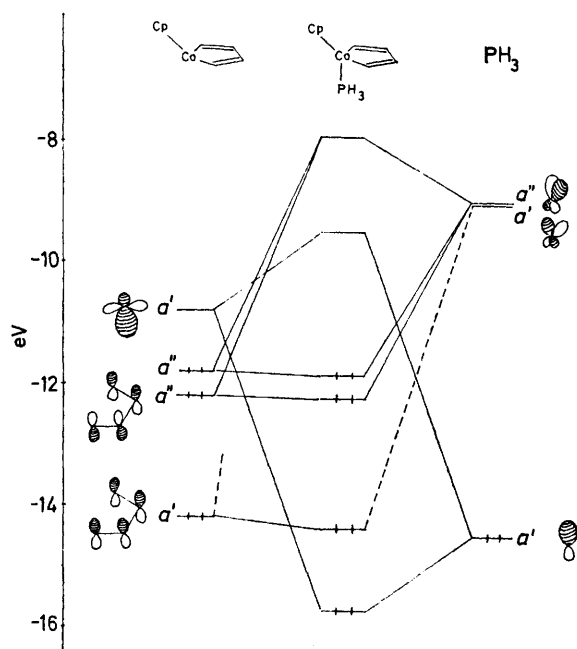

FIGURE 1   Interaction diagram for CpCo(C₄H₄) and PH₃

The construction of (1) from the CpCo(C₄H₄) fragment and the PH_3 unit is illustrated in Figure 1. In addition to HOMO–LUMO interactions between Co and P, there exist interactions between filled diene π MOs and phosphine vacant orbitals. The stabilization energy due to these extra interactions was calculated to be 0.25 eV. Therefore, 63% of the difference in the stabilization energies between (1) and (6) can be traced back to these extra interactions. The difficulty of phosphine dissociation, observed in the cases of (3) and (4), may also originate from the interaction between phosphine and the π-orbitals in the metallacycle. Why then does (5), which has similar π-orbitals in the metallacycle, lose phosphine at room temperature? The reason could be the

* For related calculations on metallacyclopentadienes, see ref. 7.

non-planer conformation of the metallacycle moiety. The folded conformation shown in Figure 2 is postulated by analogy with phenox-arsine [9] and -stibine.[10] In such a non-planer conformation, the original π-orbitals in the metallacycle are distorted away from the phosphine orbitals.

Homolytic cleavage of the metal–carbon σ-bond was considered by partitioning (1) into the CpCo(PH₃)

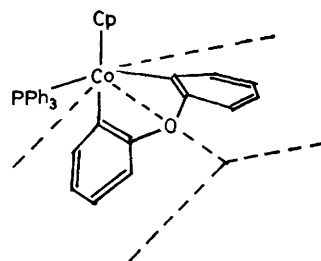FIGURE 2   Folded conformation for (5)

fragment and the C_4H_4 biradical. A similar procedure was repeated for the phosphine-free intermediate, i.e. CpCo(C₄H₄) ⟶ CpCo: + ·CH₂–CH₂CH₂–CH₂·. The stabilization energy thus evaluated indicated that the Co–C bond is stronger in the parent complex than in the phosphine-free intermediate. The same conclusion was obtained for (6) and its phosphine-free intermediate. These findings are in accord with the experimental results that the thermal decomposition of the cobalt metallacycles takes place via the phosphine-free intermediate shown in the Scheme. This tendency may be accounted for by a geometrical change which could lead to a weaker Co–C bond. Alternatively, it could be interpreted as resulting from the original quasi-octahedral conformation. Minute inspection of each MO and the interactions between them revealed that the effect of phosphine can be ascribed mostly to a change in the singly occupied MO (a') of the metal fragment. In this orbital, the bonding interaction between the cyclopentadienyl π-orbitals and the metal lobe which point to the X-direction (see Figure 3), was found to increase
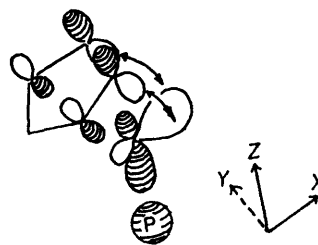
FIGURE 3   Singly occupied MO in CpCo(PH₃) fragment of a' symmetry

when phosphine is absent. Consequently, the metal lobe spreads more towards the Cp-ring (Z-direction) and shrinks from the X-direction giving smaller overlap with the two leaving carbon radicals.

Finally, the insertion step of ethylene into cobalta-cyclpentadiene and -cyclopentane, i.e. the reaction (II) ⟶ (III) in the Scheme, was simulated using models (1a)
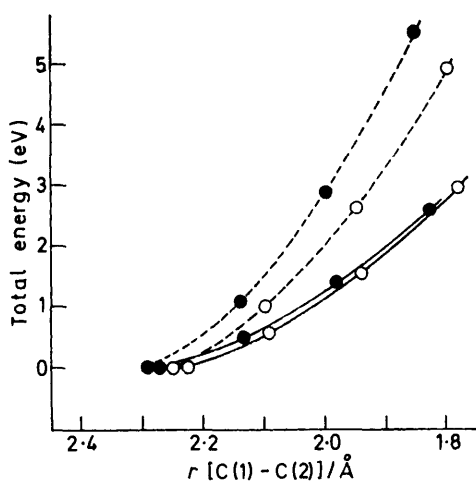
FIGURE 4 Total energy for (1a) and (6a) as a function of C(1)–C(2) distance and plotted from an arbitrary energy zero. (1a), solid lines; (6a), dashed lines; ○ ethylene oriented parallel to Co–C(2) bond; ● ethylene twisted 20° about Co–M axis

and (6a). Ethylene was initially oriented parallel to the Co–C(2) bond and then tilted by decreasing the bond angle C_2CoM, while maintaining its co-ordination to cobalt. Although the geometry of the metallacycle can differ in the initial and transition states, we expected that

(1a)   (6a)
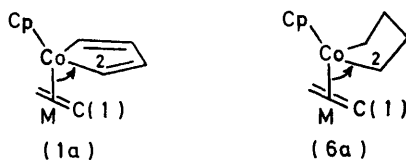
the calculations using the original geometries and then successive tilting of ethylene could provide information about the early stage of the reaction. Figure 4 shows the change of total energy as a function of the C(1)–C(2) distance. As C(1) approaches C(2), the energy is
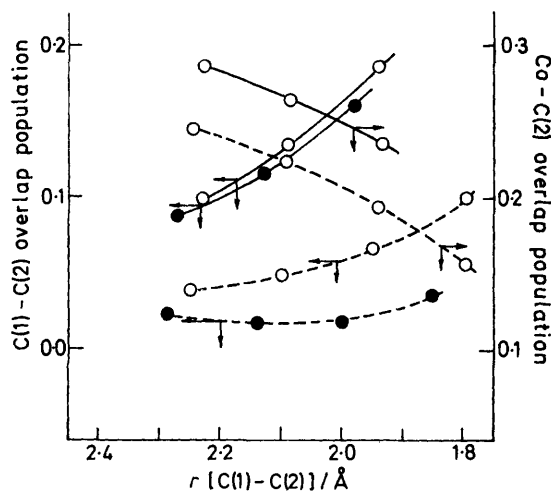

FIGURE 5 C(1)–C(2) and Co–C(2) overlap population for (1a) (solid lines) and (6a) (dashed lines) as a function of C(1)–C(2) distance: ○, ethylene oriented parallel to Co–C(2) bond; ●, ethylene twisted 20° about Co–M axis

increased more sharply in (6a) than in (1a). Further, it can be seen that twisting ethylene about the Co–M axis (20°) lead to a very slight change in (1a) but is energetically unfavourable in (6a). An indirect indication that this tendency is reasonable is found in Figure 5, which shows the evolution of the overlap populations between the relevant atoms. As the angle C(2)CoM decreases, the overlap population between C(1) and C(2) increases smoothly both in (1a) and (6a), while that of Co–C(2) [and also Co–C(1)] decreases. Twisting ethylene about the Co–M axis is again not favourable in (6a). The results shown in Figures 4 and 5 imply that cobalta-cyclopentadiene (1) is more reactive than the saturated cobalt metallocycle (6) for the insertion of olefins. Since (6a) strongly favours ethylene staying in the plane defined by C_2CoM and this requirement is not critical in (1a), the difference in reactivity for the insertion step will be enhanced when substituents on olefin or on α-carbons of the metallacycle are bulky.

EXPERIMENTAL

Reactions were carried out under nitrogen. Activated alumina (Sumitomo) was used for column chromatography.

New organic products

Compound [a]	M.p. (°C)	Analysis (%) Obs. (Calc.)		Chemical shift (δ; CDCl$_3$) [b]
(7)	141—143	C 93.0 (93.15)		0.5—2.0 (C$_4$H$_9$, m)
		H 6.89 (6.85)		
(8b)	163—166	C 84.35 (84.6)		3.59 (CO$_2$CH$_3$, s)
		H 5.2 (5.15)		
(9b)	207—211	C 90.05 (90.15)		
		H 5.3 (5.25)		
(9c)	173—175	C 80.3 (80.45)		3.40 (CO$_2$CH$_3$, s)
		H 5.1 (4.9)		
(9d)	117—118	C 70.1 (69.95)		3.86 (CO$_2$CH$_3$, s)
		H 4.6 (4.55)		
(13)	97	C 88.75 (88.7)		1.2—1.8 (CH$_2$, m)
		H 7.45 (7.45)		2.00 (CH$_3$, s)
		N 3.8 (3.85)		2.67 (CH$_3$, t)
(14)	128	C 89.1 (88.7)		
		H 6.1 (6.05)		2.02 (CH$_3$, s)
		N 4.9 (4.95)		
(15)	70—71	C 84.0 (84.25)		
		H 5.8 (5.7)		2.02 (CH$_3$, s)
		N 4.65 (4.7)		
				0.9—1.5 (CH$_2$, m)
(16)	93	C 76.2 (76.15)		2.50 (CH$_3$, t)
		H 6.9 (6.9)		3.48, 3.66 (CO$_2$CH$_3$) 4.20 (H, AB q, J_{AB} 1.8 Hz, $\delta_A - \delta_B$ 0.15 p.p.m.)

[a] Molecular weights checked by mass spectra. [b] Phenyl absorptions omitted.

C_4 and C_6 products from (6) were analysed by g.l.c. on a Shimazu GC-4CM instrument equipped with flame ionizing detectors, using a Silicon DC550 column (6 m). New organic compounds obtained in this work are listed in the Table.

Preparation of Cobaltaindene Complex (3).—To a cooled (−20°) mixture of diphenylacetylene (1.8 g, 10 mmol) and tetramethylenediamine (2.32 g, 20 mmol) was added slowly a hexane solution of Bu^{n}Li (20 mmol) with stirring. The mixture was warmed to room temperature and then added to a suspension of (C$_5$H$_5$)Co(PPh$_3$)I$_2$ (5.2 g, 8 mmol) in benzene (30 ml). After vigorous stirring for 2 h, the mixture was concentrated and chromatographed on alumina. A

brown band was eluted with benzene. Concentration of the eluate and addition of hexane gave dark brown crystals of 1-(η^3-cyclopentadienyl)-2-phenyl-3-n-butyl-1-triphenyl-phosphino-1-cobaltaindene (3) (1.76 g, 35%), m.p. 167—170 °C (decomp.) (Found: C, 79.25; H, 6.15. $C_{41}H_{38}CoP$ requires C, 79.35; H, 6.15%), $\delta(CDCl_3)$ 0.5—2.1 (m, Bu^n) and 4.66 (s, C_5H_5).

Preparation of Cobaltafluorene Complex (4).—$(C_5H_5)Co-(PPh_3)I_2$ (3.8 g, 6 mmol) was added to an ether solution of 2,2'-dilithiobiphenyl prepared by the reaction of Bu^nLi (14 mmol) with 2,2'-dibromobiphenyl (7 mmol). The mixture was stirred for 5 h. Chromatographic purification of the product as above gave crystals of (4) (1.2 g, 37%).

Preparation of Cobaltaxanthen (5).—To a mixture of 2,2'-dibromodiphenyl ether (2.3 g, 7 mmol), benzene (14 ml), and hexane (14 ml) was added a hexane solution of Bu^nLi (14 mmol). The solution was stirred for 2 h at room temperature and then was added to a suspension of $(C_5H_5)-Co(PPh_3)I_2$ (4.47 g, 7 mmol) in benzene (30 ml). The mixture was stirred for 5 h. Chromatographic work-up of the resultant dark solution gave 9-(η-cyclopentadienyl)-9-triphenylphosphino-9-cobaltaxanthen, red-brown crystals of (5) (1.5 g, 38%), m.p. 155—157 °C (decomp.) (Found: C, 76.4; H, 5.35. $C_{35}H_{28}CoOP$ requires C, 75.8; H, 5.1%), $\delta(CDCl_3)$ 5.04 (s, C_5H_5).

Decomposition of (5).—Complex (5) (125 mg, 0.225 mmol) was dissolved in benzene (10 ml) and the solution was allowed to stand for 1 week, during which a solid was precipitated. After the removal of solvent the mixture was chromatographed on alumina (1.5 × 10 cm). The column was washed with hexane and the eluate with benzene-hexane (1 : 1) was collected, from which dibenzofuran was obtained (29 mg, 76%). From a second orange-red fraction, eluted with benzene, complex (5) was recovered (30 mg, 24%).

Decomposition of (6).—A red solution of (6) (221 mg, 0.5 mmol) in benzene (10 ml) was allowed to stand at room temperature. Complex (6) decomposed gradually and the solution turned almost colourless in 2 days. The solution was analysed by g.l.c. (25 °C), using n-hexane as internal standard. Only but-1- and -2-enes were detected in 75% total yield.

Phosphine Exchange in (5).—To a solution of (5) (200 mg, 0.36 mmol) in benzene (20 ml) was added $PMePh_2$ (0.2 ml) and the mixture was left for 7 days. Chromatographic work-up of the solution gave a quantitative yield of 9-(η-cyclopentadienyl)-9-[methyl(diphenyl)phosphino]-9-cobalta-xanthen as red crystals, m.p. 128—129 °C (Found: C, 72.6; H, 5.3. $C_{30}H_{26}CoOP$ requires C, 73.15; H, 5.3%), $\delta(CDCl_3)$ 0.89 (d, J_{PH} 9 Hz, CH_3) and 4.89 (s, C_5H_5).

Reaction of Acetylenes.—As an example, the reaction of (4) with methyl phenylpropiolate is described below. A mixture of (4) (0.54 g, 1 mmol), benzene (10 ml), and PhC_2-CO_2Me (3 g) in a sealed tube was heated at 95 °C for 3 days. After concentration, the mixture was chromatographed on alumina (1.5 × 12 cm). A fraction (50 ml), eluted with benzene-hexane (10 : 1), was discarded. A second fraction, eluted with benzene-hexane (2 : 1), which came out before a brown band, was collected and concentrated. Addition of hexane to the residue yielded crystals of the phenanthrene (8b). Other reactions of the cobalt metallacycles were accomplished by similar procedures except that (5) and (6) were reacted at room temperature. The reaction of C_2H_2 with (5) or (6) was carried out by saturating a solution of (5) or (6) with C_2H_2 and keeping it in a stoppered

flask. Hexadiene from the reaction of (6) with C_2H_2 was analysed by g.l.c. (60°), using n-heptane as reference.

Reaction of Carbon Monoxide.—As an example, the reaction with (5) is described below. Cobaltaxanthen (5) (280 mg, 0.505 mmol) and benzene (25 ml) were placed in an autoclave (200 cm³). The air in the autoclave was purged by flashing CO several times. Finally a CO pressure of 45 kg cm⁻² was introduced and the system was allowed to stand at room temperature. After 1 week, the reaction mixture was chromatographed on alumina (1.5 × 13 cm). A pale yellow fraction of $CpCo(CO)_2$ was eluted with benzene-hexane (1 : 3), and an orange-brown band of unchanged (5) (32 mg) was eluted with benzene-tetrahydro-furan (20 : 1). A fraction, which came out after (5) and which was eluted with CH_2Cl_2-tetrahydrofuran (20 : 1), was collected and concentrated. Addition of hexane to the residue afforded crystals of xanthone (11) (25 mg). The reaction with (6) was conducted in a similar manner, while that with (4) was carried out at 150 °C for 5 h.

Reaction of 2,6-Dimethylphenyl Isocyanide.—A mixture of (3) (310 mg, 0.5 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (100 mg, 0.76 mmol) in benzene (15 ml) was sealed in an ampoule and heated at 110 °C for 9 h. After concentration, the mixture was chromatographed on alumina (1.5 × 10 cm) to give a yellow fraction, which was eluted with benzene-hexane (1 : 4), and a red-brown fraction eluted with benzene-hexane (1 : 2). From the yellow fraction, orange crystals of (13) were obtained, which was further purified by recrystallization from methanol (yield 79 mg). From the second red-brown fraction, (3) was recovered (90 mg). By a similar procedure, (14) was isolated as orange-yellow crystals. The reaction with (5) was carried out at room temperature for 1 week to give yellow crystals of (15).

Reaction of Olefins.—A solution of (3) (200 mg, 0.32 mmol) and dimethyl maleate (0.5 ml) in benzene (13 ml) was heated at 110 °C for 2 days. Chromatographic work-up of the mixture gave brown fraction, from which the olefin complex $(C_5H_5)Co(PPh_3)[(MeO_2C)_2C_2]$ (78 mg), was isolated. A fraction eluted by benzene-CH_2Cl_2 (1 : 1) which came out before a brown band, was collected and the solvent evaporated. On cooling a hexane solution of the residue, crystals of (16) (71 mg) were obtained. The reaction of ethylene with (6) was carried out by bubbling C_2H_4 through a toluene solution of (6) for a few minutes. The flask was then stoppered and left for 1 week. Hex-1-ene (65%) and but-1-ene (11%) were determined by g.l.c. using benzene as reference.

Calculations.—The parameters used in the extended Hückel calculations are taken from the work of Thorn and Hoffmann.[7] In this work, however, the 3d orbitals were included for phosphine with the parameters H_{ii} −7.0 eV; ζ 1.40. The following geometries were used (distance in Å): Co-P 2.20, Co-Cp 2.12, (C-C)$_{Cp}$ 1.43, C-H 0.95, P-H 1.41, Co-$\widehat{P}$-H 116.0°; for cobaltacyclopentadiene Co-C(1) 1.99, C(1)-C(2) 1.33, C(2)-C(3) 1.45, C(1)-$\widehat{Co}$-C(4) 82.4°; for cobaltacyclopentane, Co-C(1) 2.02, C(1)-C(2) 1.55, C(2)-C(3) 1.52, C(1)-$\widehat{Co}$-C(4) 76.64°, C(2)-$\widehat{C}$(1)-Co 106.8°; for co-ordinated ethylene, Co-M 1.84, C-C 1.46, C-H 0.93.

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