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COBALTACYCLOPENTADIENE COMPLEXES AS STARTING MATERIALS IN THE SYNTHESIS OF SUBSTITUTED BENZENES, CYCLOHEXADIENES, THIOPHENES, SELENOPHENES AND PYRROLES

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Metalocyclopentadiene complexes have received considerable attention as intermediates in transition metal catalyzed cyclotrimerization of acetylenes. Several groups have prepared metalocyclopentadienes and shown that they react with acetylenes to give substituted benzenes: these studies were made to determine the mechanism of this catalytic reaction[1]. Hübel <u>et.al</u>. and Muller <u>et.al</u>. have, however, used ferra- and rhoda-cyclopentadiene complexes as starting materials for preparing some 5-membered heterocyclic compounds, by replacing metal atoms in the metalocyclopentadienes by sulfur, selenium, N-R and P-Ph[2,3].

In our studies of organic synthesis using cobalt metalocycles, we have found that cobaltacyclopentadiene complexes react with nitriles, carbon disulfide and methyl isothiocyanate to give pyridines, 1,2-dithiopyrones, and N-methylthiopyridone[4]. Here, we would like to report the reaction of the cobaltacyclopentadiene complexes with acetylenes, olefins, sulfur, selenium, and nitrosobenzene. The results reported here, together with those reported previously[4], demonstrate that this type of cobalt metalocycle is useful as a starting material for the preparation of 5- or 6-membered organic ring compounds with various substituents.

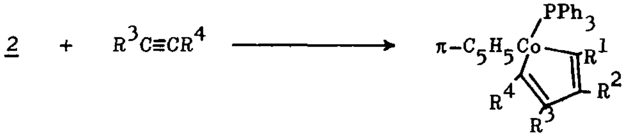
The cobaltacyclopentadiene complexes were prepared by the stepwise reactions of two molecules of an acetylene derivative with π-cyclopentadienylbis(triphenylphosphine)cobalt (<u>1</u>). It is of particular interest that this method easily provides complexes with two different acetylenes incorporated into the metalocyclopentadiene ring (cf. eq. 2). Thus <u>1</u> (0.4 mmol) reacted with an equimolar amount

$$\underset{\underline{1}}{\pi\text{-}C_5H_5Co(PPh_3)_2} + R^1C\equiv CR^2 \longrightarrow \pi\text{-}C_5H_5Co(PPh_3)(R^1C\equiv CR^2) + PPh_3 \qquad (1)$$

<u>2a</u>: R^1, R^2=Ph
<u>2b</u>: R^1=Ph, R^2=CO_2Me

of diphenylacetylene in benzene to give dark-green crystals of 2a (decomp. 140°) in 80% yield. Similarly, the reaction of 1 with methyl phenylpropiolate gave a 67% yield of dark-red crystalline 2b (decomp. 131-133°).

Previously, Yamazaki and Hagihara reported that complex 2a, which had been prepared by another method in lower yield, reacts with dimethyl acetylenedicarboxylate and phenylacetylene at room temperature to give the cobaltacyclopentadiene complexes 3f and 3j[5]. Analogous reactions were observed for other acetylene derivatives: Table 1 summarizes the cobaltacyclopentadiene complexes thus obtained. Complexes 3a~3e were prepared by the reaction of 1 with two equivalents of the respective acetylenes, the isolation of the complexes of type 2 being unnecessary and in cases of 3d and 3e difficult. The complexes 3 were purified, and when isomers were present e.g. 3c-1 and 3c-2, separated by column chromatography. These cobaltacyclopentadiene complexes are very stable and their solutions can be handled in air.



(2)

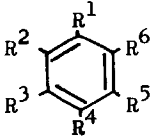
Table 1. Cobaltacyclopentadiene complexes: 3

	R^1	R^2	R^3	R^4	mp(°C)	Yield(%)*
3a	Ph	Ph	Ph	Ph	193-194	88
3b	CO_2Me	CO_2Me	CO_2Me	CO_2Me	216-217	10
3c-1	Ph	CO_2Me	Ph	CO_2Me	215-217	20
3c-2	Ph	CO_2Me	CO_2Me	Ph	218-219	13
3d-1	CO_2Me	Me	Me	CO_2Me	192-194	9
3d-2	CO_2Me	Me	CO_2Me	Me	158-160	50
3e	Ph	Me	Me	Ph	174-176	54
3f	Ph	Ph	CO_2Me	CO_2Me	119-121	48
3g	Ph	Ph	CH_2OMe	CH_2OMe	174-176	40
3h-1	Ph	Ph	Ph	CO_2Me	217-218	5
3h-2	Ph	Ph	CO_2Me	Ph	210	43
3i	Ph	Ph	Me	CO_2Me	180-182	68
3j	Ph	Ph	H	Ph	180-182	27
3k	Ph	Ph	H	p-MeC_6H_4	171	55
3ℓ	Ph	Ph	H	CO_2Me	149-151	48
3m	Ph	Ph	Me	Ph	169-171	67
3n-1	CO_2Me	Ph	Me	CO_2Me	202-203	9
3n-2	Ph	CO_2Me	Me	CO_2Me	179-182	39

* The yields of 3a~3e are based on 1, others are based on 2.

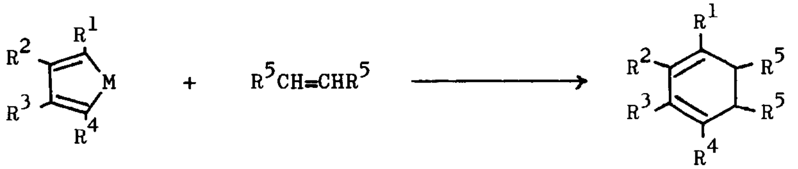
In previous work the reaction of 3a with diphenylacetylene has been shown to yield hexaphenylbenzene[1-a]. Analogous reactions between the other cobaltacyclopentadiene complexes and acetylene derivatives also proceed smoothly in benzene at 70-110°. The poly-substituted benzenes thus obtained are listed in Table 2.

Table 2. Substituted benzenes:



	R^1	R^2	R^3	R^4	R^5	R^6	mp(°C)(lit. value)	Yield(%)
4a	Ph	Ph	Ph	Ph	CO_2Me	CO_2Me	256-257(260-261)	17
4b	Ph	Ph	Ph	Ph	H	CO_2Me	195-196	22
4c	Ph	Me	Me	Ph	CO_2Me	CO_2Me	126-127	13
4d	Ph	Me	Me	Ph	H	CO_2Me	116-117(116)	26
4e	Ph	Me	Me	Ph	Ph	CO_2Me	158-160	59
4f	CO_2Me	Me	CO_2Me	Me	Ph	Ph	142-144	16
4g	Ph	CO_2Me	Me	CO_2Me	Ph	Ph	204-205	36

By using olefins instead of acetylenes, one might hope to observe a Diels-Alder reaction and thereby obtain substituted cyclohexadienes, e.g.:

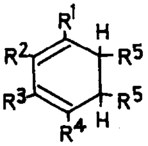


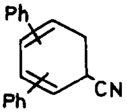
(3)

Collman et. al. and Chalk have attempted this reaction and found no reaction between olefins and an iridocyclopentadiene complex[1-b,6]. In the case of the cobaltacyclopentadienes, however, the reaction takes place in two ways depending on the reactants and reaction conditions: (A) direct production of the cyclohexadienes e.g. 3k reacted with ethylene (40 kg/cm^2) in toluene at 150° to give 5a, and (B) formation of cyclohexadiene complexes which liberate cyclohexadienes on decomposition with Ce^{4+} e.g. 3l reacted with dimethyl maleate in benzene at 110° to give a 51% yield of red crystalline π-$C_5H_5Co(C_{24}H_{22}O_6)$ which was decomposed with Ce^{4+} in benzene-ethanol solution at room temperature to give 5c in 70% yield. For phenylacetylene-acrylonitrile, the reaction proceeds catalytically in the presence of 3a (5e in Table 3).

The complexes 3 further react with sulfur, selenium, or nitrosobenzene in benzene solution at 70-110°, in the same manner as the ferracyclopentadienes[2], to give substituted thiophenes, selenophenes, and pyrroles. Table 4 shows the 5-membered heterocyclic compounds obtained in this way.

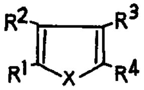
Table 3. Substituted cyclohexadienes:



	R^1	R^2	R^3	R^4	R^5	method*	mp(°C)	Yield(%)**
5a	Ph	Ph	H	p-MeC_6H_4	H	A	138.5-140	93
5b	Ph	Ph	CO_2Me	Ph	H	A	151-154	33
5c	Ph	Ph	H	CO_2Me	CO_2Me	B	117-119	36
5d	Ph	CO_2Me	CO_2Me	Ph	H	B	179-180	33
5e				(mixture of isomers)		catalytic		420

* A: obtained directly by the reaction of 3 with olefins. B: obtained by the decomposition of cyclohexadiene complex with Ce(IV). ** based on 3.

Table 4.



	R^1	R^2	R^3	R^4	X	mp(°C)(lit. value)	Yield(%)
6a	Ph	Ph	Ph	Ph	S	181(184-185)	75
6b	Ph	Me	Me	Ph	S	159	70
6c	Ph	Ph	H	Ph	S	139-140(141-142)	24
6d	Ph	Ph	CO_2Me	Ph	S	138-139(138-139)	76
6e	Ph	CO_2Me	CO_2Me	Ph	S	166-167(166-167.5)	58
6f	CO_2Me	Me	Me	CO_2Me	S	168-169(170-171)	31
6g	CO_2Me	Ph	Me	CO_2Me	S	129-131(134.5-135)	31
6h	Ph	CO_2Me	Me	CO_2Me	S	97-98	41
7a	Ph	Ph	Ph	Ph	Se	180-181(183-184)	77
7b	Ph	Me	Me	Ph	Se	156	65
7c	Ph	CO_2Me	CO_2Me	Ph	Se	174	68
8a	Ph	Ph	Ph	Ph	N-Ph	287-288(291)	34
8b	Ph	Me	Me	Ph	N-Ph	171.5-172.5	35

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