

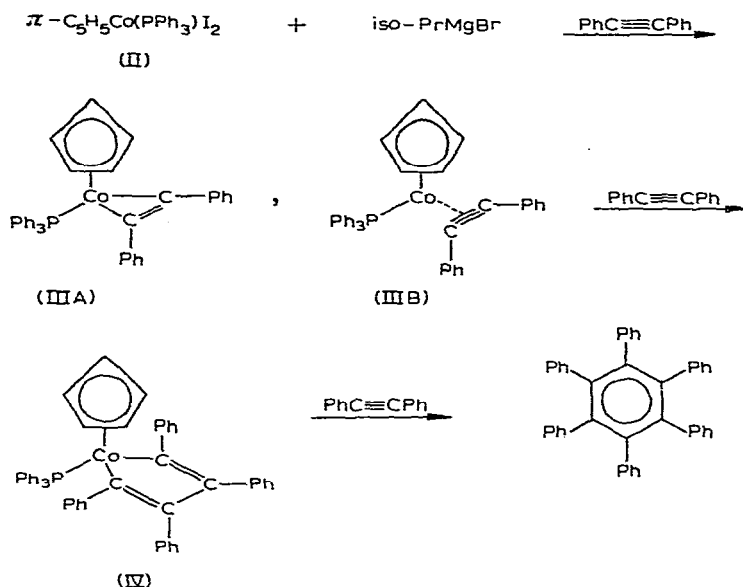
New phenylacetylene complexes of cobalt

Previously we have reported¹ the preparation of triphenylphosphine- π -cyclopentadienyldimethylcobalt (I) by reaction of triphenylphosphine- π -cyclopentadienylcobalt diiodide (II) and methylmagnesium iodide. This alkyl-cobalt complex was found to catalyze the trimerization of acetylene to benzene. In order to elucidate the catalytic process, isolation of acetylene complexes was attempted by reaction of II with isopropylmagnesium bromide in the presence of diphenylacetylene at low temperature. (It may be noted that we were not able to isolate any intermediate complexes from the cyclization of acetylene mentioned above.) Thus, to the solution of equimolar amounts of II and diphenylacetylene in tetrahydrofuran was added isopropylmagnesium bromide in ether dropwise at -15°C under nitrogen atmosphere. After hydrolysis of the resulting green-brown solution and evaporation of the solvent, the residue was separated on an alumina column using a benzene-hexane mixture as the eluant. After elution of a red fraction*, the green-colored column was eluted with benzene. Concentration of the eluate and crystallization from hexane gave black crystals of $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})$ (III), in 18% yield. (Found: C, 78.59; H, 5.37; mol.wt., 530 (cryoscopic in benzene). $\text{C}_{37}\text{H}_{30}\text{PCo}$ calcd.: C, 78.72; H, 5.36; mol.wt., 565. PMR (100 Mc. in C_6D_6 , TMS as internal standard): $\tau = \sim 3$ (broad, C_6H_5); 5.17 unresolved singlet, C_5H_5 .) III does not show any distinct melting point and gradually decomposes near 140° . It is moderately air stable in the solid state and dissolves in benzene to give dark green solutions. Reaction of III with iodine gave I and diphenylacetylene in good yield. The carbon-to-carbon stretching frequency of the acetylene linkage of III appeared at 1818 cm^{-1} , suggesting a decrease in bond order. The structure of III is suggested to be IIIA or IIIB. The coordinated diphenylacetylene of III was easily replaced by olefins with electron withdrawing substituents to give olefin complexes of type $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{RHC}=\text{CHR})$, ($\text{R} = \text{CN}$ and COOCH_3). On the other hand, addition reactions occurred with acetylenic compounds. Thus, when a mixture of III and diphenylacetylene in benzene was heated at 80° for a few minutes, very air stable, brown-red crystals of $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)(\text{PhC}\equiv\text{CPh})_2$ (IV), (60%), m.p. $193\text{--}194^{\circ}$, were obtained after chromatography on alumina. (Found: C, 82.57; H, 5.57. $\text{C}_{51}\text{H}_{40}\text{PCo}$ calcd.: C, 82.47; H, 5.43.) The PMR (60 Mc. in CDCl_3 , TMS as internal standard) showed absorption at $\tau = \sim 2.6$ (broad, $\text{P-C}_6\text{H}_5$), ~ 3.3 (complex multiplet, $\text{C-C}_6\text{H}_5$) and 5.18 (singlet, C_5H_5). IV gave π -cyclopentadienyl- π -tetraphenylcyclobutadienecobalt² in 60% yield when heated above its melting point, π -cyclopentadienyl- π -tetraphenylcyclopentadienonecobalt³ in 77% yield when treated with carbon monoxide at 100° under pressure and π -cyclopentadienyl- π -tetraphenylbutadienecobalt⁴ in 10% yield when hydrogenated with lithium aluminum hydride. Based on these reactions, a five-membered Co-containing ring structure is suggested for IV.

This compound also was prepared by the reaction of I with diphenylacetylene in benzene at reflux and by the reaction of II with isopropylmagnesium bromide in the presence of excess of diphenylacetylene at ice temperature.

Hexaphenylbenzene was produced in 8% yield when a solution of IV and diphenylacetylene in toluene was heated at reflux for one hour.

* Brown red crystals were obtained from this fraction and determination of their structure is in progress.



Although the polymerization of diphenylacetylene does not proceed catalytically, the reaction sequence mentioned above would suggest a mechanism of I-catalyzed cyclic polymerization of acetylene.

Detailed studies of the reactions of III and IV will be published in near future.

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