Reaction of Cobaltocene with Organic Compounds under an Oxygen Atmosphere: A new Route to π-Cyclopentadienyl(1-*exo*-organylcyclopentadiene)cobalt

Hidetaka Kojima, Shigetoshi Takahashi, Hiroshi Yamazaki[*1] and Nobue Hagihara

The Institute of Scientific and Industrial Research, Osaka University, Yamada-Kami, Suita, Osaka

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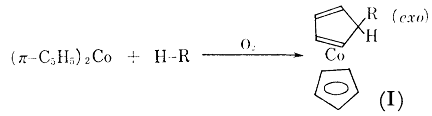
A number of π-cyclopentadienyl(1-*exo*-organylcyclopentadiene)cobalt complexes have been prepared by the reaction of organic halides with cobaltocene,[1] or organic alkali metals with cobalticenium perchlorate.[2]

We wish to report here a new reaction of cobaltocene with organic compounds having an active hydrogen atom under an oxygen atmosphere, which gives π-cyclopentadienyl(1-*exo*-organylcyclopentadiene)cobalt complexes in a high yield.



(I)

Oxygen was bubbled continuously through a dark red solution of cobaltocene in chloroform. After one hour, chloroform was removed from the resulting solution under reduced pressure to give orange red crystals of π-cyclopentadienyl(1-*exo*-trichloromethylcyclopentadiene)cobalt (Ia). The IR and NMR spectra and the melting point were identical with those of the authentic sample which was prepared by the reaction of cobaltocene with carbon tetrachloride.[3] Almost quantitative yield of Ia is a characteristic point of our method. In the case of the reaction of cobaltocene with carbon tetrachloride, the yield can not exceed 50% stoichiometrically, because half of the cobaltocene is consumed for the formation of cobalticenium chloride.

In the same way, cobaltocene reacted very smoothly with acetonitrile, propionitrile, phenylacetylene and acetone to form new complexes, $(\pi\text{-}C_5H_5)Co(C_5H_5\text{-}CH_2CN)$, $(\pi\text{-}C_5H_5)Co(C_5H_5\text{-}CH(CN)CH_3)$, $(\pi\text{-}C_5H_5)Co(C_5H_5\text{-}C{\equiv}CC_6H_5)$ and a new binuclear complex, $(\pi\text{-}C_5H_5)Co(C_5H_5\text{-}CH_2\text{-}COCH_2\text{-}C_5H_5)Co(\pi\text{-}C_5H_5)$. These complexes are summarized in Table 1.

Weiher *et al.*[4] reported smooth absorption of one mole of oxygen by four moles of cobaltocene at 0°C. They were unsuccessful in isolating and characterizing the oxygenated product. We observed that an orange solid was precipitated by the treatment of a solution of cobaltocene in ether with oxygen at −50°C. When chloroform was added to the orange solid suspended in ether under a nitrogen atmosphere, the solid was dissolved, the color of the solution turned to red, and the complex $(\pi\text{-}C_5H_5)Co(C_5H_5\text{-}CCl_3)$ was isolated in a 95% yield. This suggests that the oxygenated cobaltocene is an intermediate in the new reaction of cobaltocene. More detailed studies on the reaction mechanism are in progress.

TABLE 1. CYCLOPENTADIENYL(1-*exo*-ORGANYLCYCLOPENTADIENE)COBALT COMPLEXES*

Complex		H–R	Yield (%**)	Mp (°C)	Color
Ia	R=$-CCl_3$	$CHCl_3$	97	80—81	orange red
Ib	R=$-CH_2CN$	CH_3CN	87	58	red
Ic	R=$-CH(CN)CH_3$	CH_3CH_2CN	51	84—85	red
Id	R=$-C{\equiv}CC_6H_5$	$HC{\equiv}CC_6H_5$	56	130 (decomp.)	orange red
II***	R=$-CH_2COCH_2-$	CH_3COCH_3	70	100 (decomp.)	orange

* Satisfactory data of elemental analysis were obtained for all the new complexes.

** Based on cobaltocene. *** Binuclear complex.

[*1] Present address: The Institute of Physical and Chemical Research, Yamatomachi, Saitama.

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