Cyclopentadienyl Cobalt Cyclooctatetraene

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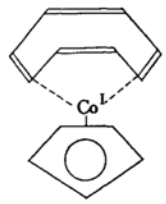
The present authors have previously reported the synthesis of cyclooctatetraene iron tricarbonyl and related compounds[1]. In continuation of the present study, the authors now wish to report a new synthesis of cyclopentadienyl cobalt cyclooctatetraene. Cyclopentadienyl cobalt dicarbonyl was heated at reflux in an excess of cyclooctatetraene under nitrogen for 6 hr. After removal of the unreacted starting materials, brown crystals were obtained by sublimation at 80°C under reduced pressure in 7% yield. These crystals were purified by recrystallization from petroleum ether and by sublimation. The purified sample had a m. p. of 81~82°C. Found: C, 68.32; H, 5.66; mol. wt. (Rast), 256. Calcd. for $C_{13}H_{13}Co$: C, 68.42; H, 5.74%, mol. wt., 228.



(I)

The elemental analysis apparently conformed to the structure, $(C_5H_5)Co(C_8H_8)$, cyclopentadienyl cobalt cyclooctatetraene (I). The same compound (I) could be obtained by irradiation of a mixture of cyclopentadienyl cobalt dicarbonyl and cyclooctatetraene with ultraviolet light under nitrogen for many hours.

I was soluble in common organic solvents and was stable in air. It was also soluble in cold concentrated sulfuric acid and in warm concentrated hydrochloric acid. The solution of I in carbon tetrachloride was decomposed by bromine and by iodine to give green and black precipitates, respectively. I reacted with cyclopentadienyl cobalt dicarbonyl in refluxing dioxane to give dark brown crystals, m.p. >300°C (with decomposition). I readily absorbed 2 mol. of hydrogen in the presence of Raney nickel catalyst at room temperature under ordinary pressure. Orange crystals, m.p. 102°C, were isolated from the hydrogenation mixture by sublimation in a reduced pressure at 80°C. These products of the reaction of I with bromine, iodine, hydrogen, cyclopentadienyl cobalt dicarbonyl and other reagents are now being studied in this laboratory and the results will be reported at a later date.

Three distinct proton resonance peaks were found at 82, 123 and 159 c. p. s, (ratio of the areas; 4.1 : 5 : 4.1), respectively, on the low field side from the proton resonance of cyclohexane. The result of this nuclear magnetic resonance study indicates that three different kinds of protons are present in I in a ratio of 4 : 5 : 4.

The infrared spectrum of I (in Nujol) showed a strong band at 1637 cm^{-1} due to C=C stretching similar to the corresponding 1635 cm^{-1} band of cyclooctatetraene. In the ultraviolet region it had an absorption maximum at 245 mμ ($\log \varepsilon$: 4.32, in 95 % alcohol).

These spectral and NMR data together with the chemical reactivity of I are essentially different from those of cyclooctatetraene iron tricarbonyl[1-3]. The double bonds in I which are presumably not used in π-bonding with the cobalt show usual properties of olefinic double bonds as described above. In contrast to this fact all four double bonds of the cyclooctatetraene moiety in cyclooctatetraene iron tricarbonyl do not show the usual properties of double bonds and they were thought to be affected by π-complex formation[3]. Accordingly the cyclooctatetraene moiety in I should be different from that of cyclooctatetraene iron tricarbonyl in its spacial and electronic structures. From the above evidences the authors propose the structure shown in the figure for I.

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