New Stable Olefin Complexes of Cobalt(I)

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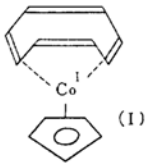
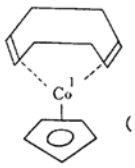
In a previous communication the authors described the synthesis of cyclopentadienyl cobalt cyclooctatetraene (I)[1]. In that report the authors reported that I took up 2 mol. of hydrogen on catalytic hydrogenation to give orange crystals (II), m. p. 102°C. The authors supposed this compound II to be cyclopentadienyl cobalt 1, 5-cyclooctadiene considering from the proposed structure of I (cf. Fig. 1). In order to determine the correct structure of II, an attempt was made to obtain the same compound from 1, 5-cyclooctadiene. Thus 1, 5-cyclooctadiene was refluxed with cyclopentadienyl cobalt dicarbonyl in xylene under nitrogen for 15 hr. After removal of the unreacted starting materials, orange crystals were obtained by sublimation at 80°C under reduced pressure in 30% yield. These crystals were recrystallized from petroleum ether, m. p. 102.5°C. Found: C, 67.05; H, 6.76. Calcd. for $C_{13}H_{17}Co$: C, 67.24; H, 7.38%. The infrared spectrum of this compound was identical with that of II and showed the presence of π-cyclopentadienyl group. No absorption was observed at usual C=C stretching region. These facts indicate the structure of II to be $(C_8H_{12})Co(C_5H_5)$ which is shown in Fig. 2.



(I)

Fig. 1



(II)

Fig. 2

1, 3, 5-Cyclooctatriene yielded brown crystals (III), m. p. 90°C, by the similar reaction with cyclopentadienyl cobalt dicarbonyl. The infrared spectrum of III showed C=C stretching absorption at 1625 cm.$^{-1}$ III also gave II on catalytic hydrogenation.

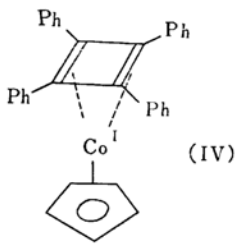
II was stable in air, soluble in organic solvents and readily decomposed by bromine or by iodine in carbon tetrachloride. It also reacted with carbon monoxide (50 atm.) to give cyclopentadienyl cobalt dicarbonyl. The ultraviolet spectrum of II showed maximum at 361 mμ(log ε: 2.87, in alcohol) and had shoulders at 235, 267 and 420 mμ, as well as increasing absorption in the shorter wavelengths. I and II reacted with diphenyl acethylene in refluxing xylene to give yellowish brown crystals (IV), m. p. 256°C, in 40 and 47% yield respectively. These crystals were purified by recrystallization from benzene or by chromatography on alumina. Found: C, 81.82; H, 5.2. Calcd. for $C_{33}H_{25}Co$: C, 82.48; H, 5.24%. The analysis conformed to the composition, $(C_5H_5C{\equiv}CC_6H_5)_2Co(C_5H_5)$. IV was soluble in organic solvents and was quite stable in air. IV was thermally stable up to ca. 360°C under nitrogen and surprisingly oxidation resistant as a univalent cobalt compound. For example the solution of IV in benzene was oxidized neither by air on heating nor by iodine on warming. The ultraviolet spectrum of IV showed maxima at 241, 257 and 278 mμ (log ε: 4.51, 4.50, 4.46, in alcohol) and had shoulders at 287, 295 and 400 mμ.

The infrared spectrum of IV showed the

1) A. Nakamura and N. Hagihara, This Bulletin, 33, 425 (1960).

presence of π-cyclopentadienyl group and mono-substituted phenyl group.

IV was reduced by sodium in liquid ammonia to give 1, 2, 3, 4-tetraphenylbutane, m. p. 181°C. IV did not react with concentrated hydrochloric acid, alcoholic potassium hydroxide and lithium aluminum hydride. It was attacked neither by carbon monoxide (100 atm.) at 290°C, by triphenyl phosphine at 150°C nor by acetylene dicarboxylic acid ester at 200°C. This remarkable stability of the compound IV together with its chemical and spectroscopic properties seems to indicate its structure involving a cyclobutadiene ring as shown in Fig. 3. Alternative structures such as those involving Co–C sigma bonds or involving tetraphenylbutadiene are less probable.



(IV)

Fig. 3

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