

BENZENE COMPLEXES IN CYCLOPENTADIENYLCOBALT(I) REACTION SYSTEMS

WAI-SUN LEE, JOHNSON D. KOOLA and HANS H. BRINTZINGER

Fakultät für Chemie, Universität Konstanz, 7750 Konstanz (Bundesrepublik Deutschland)

Summary

Photolysis of $(C_5H_5)Co(CO)_2$ in an aromatic solvent, such as benzene, toluene or *s*-mesitylene generates the corresponding $(C_5H_5)Co(\text{arene})$ and $(C_5H_5)Co(\text{arene})_2$ complexes. The benzene complex $(C_5H_5)Co(C_6H_6)$ reacts with 2-butyne to form the hexamethyl benzene derivative $(C_5H_5)Co(C_6(CH_3)_6)$ but does not catalyze the formation of free hexamethylbenzene from excess 2-butyne.

Photochemical reactions of $(C_5H_5)Co(CO)_2$ have been studied by a number of research groups in considerable detail [1–3]. The generation of coordinatively unsaturated intermediates in systems of this kind usually results in the formation of bi- and polynuclear $(C_5H_5)Co^I$ clusters. In an attempt to observe primary intermediates in these photoreaction sequences, we have photolysed rather dilute $(C_5H_5)Co(CO)_2$ solution was filtered from the polynuclear species should be disfavored. Unexpectedly, we have observed that complexes of $(C_5H_5)Co^I$ with aromatic solvent molecules are formed under these conditions.

In a typical experiment, a solution of 500 mg of $(C_5H_5)Co(CO)_2$ in 120 ml of benzene was photolysed at room temperature with a high-pressure mercury lamp, the evolved CO being pumped off from time to time. After about 12 hours, when evolution of CO had ceased, the solution was filtered from the precipitated substances and evaporated to yield an oily residue, which was taken up in petroleum ether, and the solution was filtered and evaporated again. The oily residue is shown by mass spectral analysis to consist of a mixture of $(C_5H_5)Co(C_6H_6)$ (Ia) and $(C_5H_5)Co(C_6H_6)_2$ (IIa). Both compounds are very soluble in all organic solvents and easily sublimable at 30–40°C. By repeated fractional sublimation, Ia and IIa can be largely but not completely purified. $(C_5H_5)Co(C_6H_6)$ is obtained in this manner as a yellow liquid and

efficient cyclotrimerization catalysis exerted by a number of $(C_5H_5)CoI$ derivatives*. Whether a coligand, such as phosphine or CO is required for an effective catalytic turnover, or whether a binuclear metallocyclic compound, such as $(C_5H_5)_2Co_2(C_4(CH_3)_4)[7,10]$, is a necessary intermediate for such a catalytic reaction, remains to be clarified.

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*Complexes of the type reported here are also likely to be formed in the photolytic or thermal degradation of polystyrene-supported cyclopentadienylcobalt dicarbonyl derivatives, in which the site-isolation effect of the polystyrene matrix [8,9] duplicates the situation of the very dilute solutions employed in this study. Significantly, Perkins and Vollhardt [9] have reported that polystyrene-supported C_5H_5CoI species of this type are similarly inactive in alkyne cyclotrimerisation.