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Preliminary communication

BENZENE COMPLEXES IN CYCLOPENTADIENYLCOBALT(I) REACTION SYSTEMS

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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(arene) and (C_5H_5)Co(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

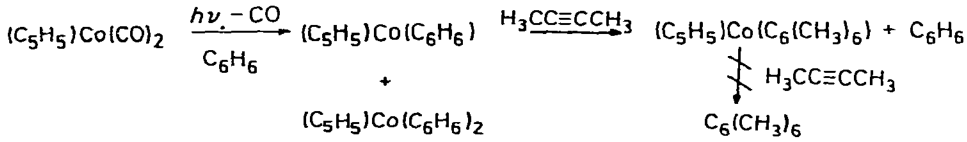
$(C_5H_5)Co(C_6H_6)_2$ as a brown solid, both in very small yields (ca. 2—5% based on $(C_5H_5)Co(CO)_2$). In the mass spectrum of $(C_5H_5)Co(C_6H_6)$ one observes, besides the parent ion at $m/e = 202$, mainly the fragment $(C_5H_5)Co^+$ ($m/e = 124$); in that of $(C_5H_5)Co(C_6H_6)_2$ the parent ion M^+ at $m/e = 280$ and the fragments $(M - 2H)^+$, $(M - 2H - C_5H_5)^+$, $(M - C_6H_6)^+$ and $(C_5H_5)Co^+$ at m/e = 278, 213, 202 and 124, respectively.

Completely analogous observations and products were obtained with toluene and with s-mesitylene as solvents, the yields of $(C_5H_5)Co(s\text{-}C_6H_3(CH_3)_3)$ and $(C_5H_5)Co(s\text{-}C_6H_3(CH_3)_3)_2$ being about double those obtained with benzene.

The formation of these (C_5H_5)Co(arene) and (C_5H_5)Co(arene)$_2$ complexes is in line with a report by King et al. on the isolation of the two complexes $(C_5(CH_3)_5)Co(C_6(COOCH_3)_6)$ and $(C_5(CH_3)_5)Co(C_6(COOCH_3)_6)_2$ [4]. In all of these (C_5H_5)Co(arene) species, the arene ligand is probably bound to the metal center in an η^4-coordination, whereas for the (C_5H_5)Co(arene)$_2$ compounds an η^2-coordination of the arene rings is to be expected from the 18-electron rule*.

All the (C_5H_5)Co(arene)$_n$ compounds obtained are stable in air at room temperature, and at temperatures around 100°C in vacuo.

The reactivity of (C_5H_5)Co(arene) complexes is of considerable interest, since (C_5H_5)Co-derivatives are catalytically active in the cyclotrimerization of alkynes to aromatic compounds [5—7]. In order to establish whether (C_5H_5)Co(arene) species are intermediates in these catalytic alkyne reaction sequences, we investigated the reaction of $(C_5H_5)Co(C_6H_6)$ with 2-butyne. A solution of 40 mg (0.2 mmol) of the benzene complex in about 10 ml toluene, containing 5.0 mmol of $CH_3C{\equiv}CCH_3$, was heated to 100°C for 20 hours in a pressure-resistant reaction vessel. After removal of solvent and excess 2-butyne, the mass spectrum of the residue revealed the complete disappearance of the original $(C_5H_5)Co(C_6H_6)$; instead there was a strong peak at $m/e = 316$, assignable to the hexamethylbenzene complex $(C_5H_5)Co(C_6(CH_3)_6)$. Free hexamethylbenzene, however, was not detectable in the reaction residue in any significant amount.



From these observations, we conclude that $(C_5H_5)Co(C_6H_6)$ is reactive enough, at the elevated temperatures employed, to allow the alkyne substrate to coordinate to, and to cyclotrimerize at the cobalt center; the increased stability of the hexamethylbenzene complex formed, however, then appears to block further access of the alkyne to the metal center. It would thus seem that (C_5H_5)Co(arene) complexes cannot be involved as intermediates in the

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*Alternatively, the C_5H_5 ligand could be present in an η^3-coordination. In trying to settle this point, we were unable to obtain satisfactory NMR spectra for any of the arene complexes described; this may be due either to incomplete separation or to some enhanced line broadening as a result of the structural fluxionality to be expected for these compounds.

efficient cyclotrimerization catalysis exerted by a number of $(C_5H_5)Co^I$ 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 $C_5H_5Co^I$ species of this type are similarly inactive in alkyne cyclotrimerisation.