

Preliminary communication

$[(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$: A probable intermediate in the cyclization of acetylenes by $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$

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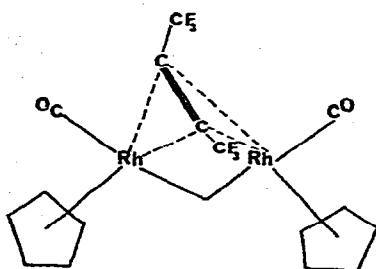
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The reactions of acetylenes with π -cyclopentadienyldicarbonylcobalt, $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, have given π -cyclopentadienyl- π -cyclobutadienecobalt^{1,2} and/or π -cyclopentadienyl- π -cyclopentadienonecobalt²⁻⁴ complexes. Similar reactions involving π -cyclopentadienyldicarbonylrhodium, $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$, have produced π -cyclopentadienyl- π -tetrahapto-benzenerhodium⁵ and/or π -cyclopentadienyl- π -cyclopentadienone-rhodium^{5,6} complexes.

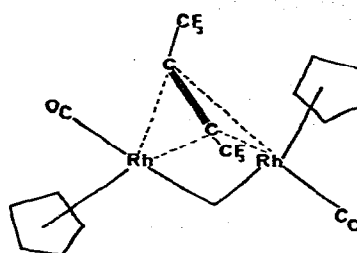
The formation of these cyclic ligands from acetylenes presumably involves organometallic intermediates incorporating acetylene molecules as recognizable entities. Complexes of this type have not been isolated from reactions involving $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, but Rausch and co-workers have reported briefly⁷ on the complexes $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)_2$ and $[(\pi\text{-C}_5\text{H}_5)\text{Rh}]_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ which are formed in the reaction between $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ and bis(pentafluorophenyl)acetylene. We report here on the formation and characterization of a related complex in which the acetylene molecule, $\text{CF}_3\text{C}\equiv\text{CCF}_3$, acts as a bridging group between two rhodium atoms.

In a previous study⁵ of the reaction between $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ and hexafluoro-2-butyne, Dickson and Wilkinson reported the formation of π -cyclopentadienyl- π -tetrakis-(trifluoromethyl)cyclopentadienonerhodium and π -cyclopentadienyl- π -hexakis-(trifluoromethyl)benzenerhodium. We have now isolated bis(π -cyclopentadienylcarbonylrhodium)hexafluoro-2-butyne, $[(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$, as orange-red crystals (m.p. 162–163°C) from the same reaction system in hexane as solvent. The formulation of the complex is indicated by elemental and mass spectral analysis. The IR and NMR spectra of the complex are consistent with a stereochemistry (I) or (II). The suggested structure is thus closely related to the known structures of the bridging acetylene complexes $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ ⁸ and $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ ^{9,10}.

The ¹⁹F NMR spectrum of the Rh complex shows only one sharp singlet at δ 54.37 ppm upfield from CCl_3F which is consistent with a symmetrical arrangement of the $\text{CF}_3\text{C}\equiv\text{CCF}_3$ bridging group. The $\pi\text{-C}_5\text{H}_5$ protons resonate as a sharp singlet at τ 4.47 ppm. The IR spectrum in the carbonyl stretching region of solutions of the complex in cyclohexane displays one sharp peak at 2003 cm^{-1} . There is a hint of a weak shoulder at 1989 cm^{-1} but this could not be resolved even when the spectrum was recorded with an



I



II

expanded scale. Manning and co-workers have discussed^{11,12} the IR spectra of the *cis*- and *trans*-isomers of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ which has a structure very similar to that proposed for the present complex. The isomers of the iron complex can be identified by consideration of the positions and relative intensities of the symmetric and the asymmetric CO stretching frequencies. The appearance of only one band in the solution spectrum of the rhodium complex presumably indicates that only one isomer is present, and the position of the weak shoulder relative to the intense peak may be more consistent with a *cis*-arrangement of the terminal CO groups.

The isolation of the complexes $[(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$ and $[(\pi\text{-C}_5\text{H}_5)\text{Rh}]_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ may provide a clue to the mechanism of formation of cyclic ligands from acetylenes. Thus these bimetallic complexes rather than previously presumed⁴ intermediates of the type $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{RC}\equiv\text{CR})_2$ may be involved in the cyclic oligomerization process. With this idea in mind, the chemical behaviour of $[(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$ is being investigated.

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