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Preliminary communication

CYCLOTRIMERIZATION OF ACETYLENIC COMPOUNDS WITH (BENZENE)(1,3-CYCLOHEXADIENE)RUTHENIUM(0): PREPARATION OF BIS-ARENE DERIVATIVES OF RUTHENIUM HAVING DIFFERENT ARENE LIGANDS

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Summary

The reaction between (benzene)(1,3-cyclohexadiene)ruthenium(0) and acetylenes $RC{\equiv}CR$ under UV irradiation yields complexes of the formula $(C_6R_6)_2Ru$ or $(C_6H_6)(C_6R_6)Ru$, depending on the acetylene used.

It is well known that acetylenes can be cyclooligomerized in the presence of transition metal compounds. In many cases the cyclooligomerization products are formed as η-complexes with the transition metal: several arene and cyclobutadiene complexes have been produced in this way [1].

We now report the formation of some bis-areneruthenium(0) complexes via the cyclotrimerization of acetylenic compounds by (benzene)(1,3-cyclohexadiene)ruthenium(0). Depending on the acetylenic compound used, the reaction can yield, bis-arene derivatives having two different arene molecules coordinated to the same ruthenium atom.

Treatment of $(C_6H_6)(C_6H_8)Ru$ (I) with an excess of an acetylenic compound (molar ratio 1/10) in n-hexane at 40°C for 1—2 days, under UV irradiation gave the bis-arene complexes II. No catalytic trimerization of the acetylenic compound was observed. UV irradiation appeared necessary for the reactions.

$$\begin{tikzcd}
 & \begin{array}{l}(C_6H_6)(C_6R_6)Ru \\ (\text{IIa}, R = C_6H_5, \text{yield } 50\%) \\ (\text{IIb}, R = COOCH_3, \text{yield } 20\%)\end{array} \\
\underset{(\text{I})}{(C_6H_6)(C_6H_8)Ru} \arrow[ru, "RC\equiv CR"] \arrow[rd, "\text{UV irradiation}"'] & \\
 & \begin{array}{l}(C_6R_6)_2Ru \\ (\text{IIc}, R = CH_3, \text{yield } 40\%)\end{array}
\end{tikzcd}$$

Complexes II are orange-red diamagnetic compounds, which were characterized by elemental analysis, IR, ^{1}H NMR and mass spectra. IIa and IIb are the first examples of bis-areneruthenium(0) complexes having two different arenes coordinated to the same Ru atom; IIc is the well-known bis(hexamethy benzene)ruthenium(0) [2].

The ^{1}H NMR spectra of IIa and IIb at 35°C show a single peak due to the benzene protons (Table 1) which indicates that in these complexes the benzene ring is η^6-bonded to the ruthenium atom. From the spectra it appears that the substituted benzene is η^4-bonded in both complexes. In the case of IIa this has been confirmed by determination of the molecular structure by single crystal X-ray examination [3].

TABLE 1

NMR DATA FOR RU(BENZENE)(ARENE) COMPLEXES[a]

Compound	Benzene resonances	Arene resonances
$Ru(C_6H_6)[C_6(C_6H_5)_6]$[b]	4.90(s)	from 2.50 to 3.40
$Ru(C_6H_6)[C_6(COOCH_3)_6]$[c]	4.37(s)	6.20(s), 6.37(s), 6.42(s)

[a] Proton chemical shifts (τ, ppm) measured at MHz relative to internal TMS. [b] In $CDCl_3$ at ca. 35°C. [c] In CD_3COCD_3 at ca. 35°C.

The reaction of I with phenylacetylene and 2-butyne-1,4-diol under UV irradiation was also examined. From phenylacetylene a product of the formula $Ru[C_6H_3(C_6H_5)_3]_2$ was obtained, which was difficult to purify, presumably because several isomers were present. From butyne-1,4-diol an insoluble product was obtained, which could not be purified and which was tentatively assigned the formula $Ru(C_6H_6)[C_6(CH_2OH)_6]$ on the basis of elemental analysis. The reaction of I with acetylene was also examined, no pure product was isolated.

No reaction was observed between I and several substituted benzenes under UV irradiation at temperatures up to ca. 100°C.

The reaction of I with an acetylene RC≡CR, under UV irradiation first yields the complex $(C_6H_6)(C_6R_6)Ru$, which, depending on the acetylenic compound used, can further react to give $(C_6R_6)_2Ru$. Since I can be easily obtained [4], the reaction offers a convenient route to new bis-arene derivatives of ruthenium(0).

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References

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